

Synthesis of Surface-Metallized Polyimide Films via in Situ Reduction of (Perfluoroalkanoato)silver(I) Complexes in a Poly(amic acid) Precursor

Robin E. Southward,^{*,†} Christopher M. Boggs,[‡] David W. Thompson,^{*,‡} and Anne K. St. Clair[§]

Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23187, and Materials Division, National Aeronautics and Space Administration, Langley Research Center, Hampton, Virginia 23681

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Thermal curing of the silver(I)-containing poly(amic acid) formed from 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) and 4,4'-oxydianiline (4,4'-ODA) in dimethylacetamide leads both to polyimide films via cyclodehydration and to reduction of silver(I) giving a metallized surface. The resulting metallized composite films retain mechanical and thermal properties similar to those of the parent polyimide. Variation of the silver(I) additive and concentration and the thermal cure cycle allows the fabrication of silver layers which are both reflective and/or electrically conductive. Silver(I) trifluoroacetate and pentafluoropropanoate give excellent silvered films; however, higher perfluoroalkanoates such as silver(I) heptafluorobutanoate give films which are poorly surface metallized and extensively bubbled. X-ray diffraction shows crystalline face-centered cubic silver in the films after thermal curing. Microscopy data show that the surface particle sizes are in the range of ca. 100–500 nm. Significant silver remains in the bulk of the polyimide film with varying particle sizes generally less than ca. 15 nm. The interior of the metallized films is not electrically conducting. Films were characterized by X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis, X-ray photoelectron spectroscopy, transmission electron microscopy, scanning electron microscopy, and atomic force microscopy.

Introduction

There is intense interest in the synthesis and properties of metal clusters and colloids prepared in both aqueous and organic solutions and prepared in a condensed state using polymers, surfactants, zeolites and other molecular sieves, and glasses as stabilizing matrixes.¹ Clusters and cluster-containing materials are potentially useful as highly active catalysts,² as magnetic materials,³ as quantum dots and for miniaturization of electronic devices,^{4,5} and as nonlinear optical materials.^{6,7}

We have investigated the thermally induced reduction of positive valent silver in polymeric matrixes with the concomitant formation of metal clusters.^{8–12} During

reduction a portion of the metallic phase separates to the surface to yield composite polymeric films which exhibit high specular reflectivity and, at times, surface conductivity. The native metal remaining in the bulk of the film exists as particles with sizes in the range of ca. 2–20 nm. Silver is of interest to us because of its high reflectivity and low resistivity. Aromatic poly(amic acid)–polyimide systems are polymers of choice because of their outstanding chemical and thermal stability.^{13,14} Such stability is essential since metallic Ag catalyzes air oxidation of organic moieties at the cure temperatures required to produce metallized films.¹⁵ Applications for silver-metallized polymeric films include contacts in microelectronics,¹⁶ highly reflective thin film reflectors and concentrators in space environments for

[†] National Research Council Postdoctoral Associate, NASA–Langley Research Center.

[‡] College of William and Mary.

[§] NASA–Langley Research Center.

(1) *Clusters and Colloids: From Theory to Applications*; Schmid, G., Ed.; VCH: Weinheim, 1994.

(2) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693–2730.

(3) (a) Roost, N.; Ackermann, L.; Pacchioni, G. *Chem. Phys. Lett.* **1992**, *93*, 94. (b) Ackermann, L.; Rosch, N.; Dunlap, B. I.; Pacchioni, G. *Int. J. Quantum Chem. Quantum Chem. Symp.* **1992**, *26*, 605.

(4) Halperin, W. P. *Rev. Mod. Phys.* **1986**, *58*, 533–606.

(5) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.

(6) (a) Ricard, D.; Poussignol, Ph.; Flytzanis, Chr. *Opt. Lett.* **1985**, *10*, 511. (b) Hache, F.; Ricard, D.; Flytzanis, C. *J. Opt. Soc. Am. B.* **1986**, *3*, 1647.

(7) Stucky, G. D.; MacDougall, J. E. *Science* **1990**, *247*, 669.

(8) Southward, R. E.; Thompson, D. S.; Thompson, D. W.; St. Clair, A. K. *Chem. Mater.* **1997**, *9*, 1691.

(9) Southward, R. E.; Thompson, D. S.; Thompson, D. W.; Caplan, M. L.; St. Clair, A. K. *Chem. Mater.* **1995**, *7*, 2171.

(10) Linehan, M.; Stoakley, D. M.; St. Clair, A. K. Synthesis and Characterization of Silver Nitrate-Doped Polyimide Films. *Abstracts of Papers, 44th Southeastern-26th Middle Atlantic Combined Regional Meeting of the American Chemical Society, Arlington, VA.*; American Chemical Society: Washington, DC, 1992; POLY 378.

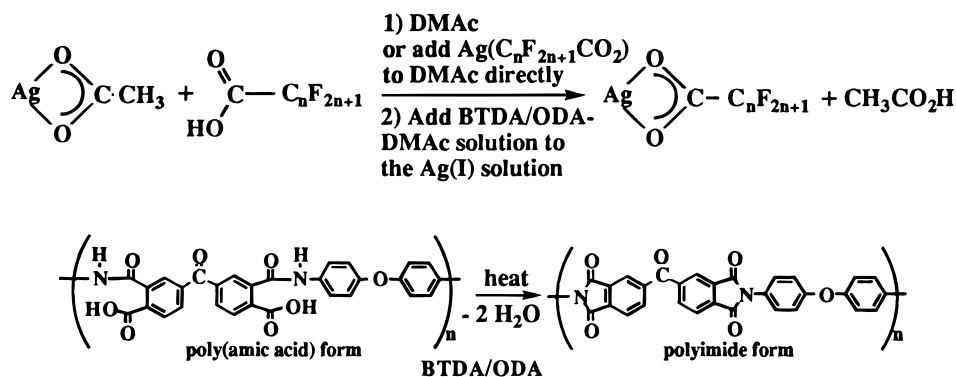
(11) Southward, R. E.; Thompson, D. S.; Thompson, D. W.; Caplan, M. L.; St. Clair, A. K. *Metal-Containing Polymeric Materials*; Pittman, C. U.; Carraher, C. E.; Culbertson, B. M.; Zeldin, M.; Sheets, J. E., Eds.; Plenum: New York, 1996, pp 349–356.

(12) Southward, R. E.; Thompson, D. W.; St. Clair, A. K. *Chem. Mater.* **1997**, *9*, 501–509.

(13) Bower, G. M.; Frost, L. W. Aromatic Polyimides *J. Polym. Sci., A* **1963**, *1*, 3135.

(14) Sroog, C. E.; Endrey, A. L.; Abramo, S. V.; Berr, C. E.; Edwards, W. M.; Olivier, K. L. *J. Polym. Sci., A* **1965**, *3*, 1373.

Scheme 1



solar thermal propulsion¹⁷ and solar dynamic power generation,¹⁸ large scale radio frequency antennas for space applications,¹⁹ bactericidal coatings,²⁰ surface conductive flexible polymeric tapes,²¹ and materials for the construction of adaptive and elastomeric optical devices.^{22,23} Polymeric supports for reflectors offer advantages in weight, flexibility, elasticity, and fragility relative to traditional supports such as glasses and ceramics.

Specifically, the research described herein focuses on the formation of metallic Ag on polyimide substrates by a single-stage, internal, in situ, self-metallization process. Our approach is illustrated in Scheme 1. Ag(I) perfluoroalkanoate is dissolved in dimethylacetamide (DMAc), or alternatively, Ag(I) acetate is allowed to react with a perfluoroalkanoic acid in DMAc which generates Ag(I) perfluoroalkanoate. A DMAc solution of the poly(amic acid) form of BTDA/ODA is added to the solution of a Ag(I) perfluorocarboxylate precursor. A film is then cast. Thermal curing of the Ag(I)-doped poly(amic acid) film effects both amic acid ring closure to give the polyimide and reduction of Ag(I) to the native metal. During thermal treatment a portion of the Ag(0), formed in the matrix of the polymer, migrates to the film surface. Characterization of these metallized films with respect to reflectivity, resistivity, thermal, mechanical, and surface properties will be detailed.

Methods commonly used to prepare metallic films involve external deposition of metal onto a substrate.

Such techniques include physical vapor deposition, chemical vapor deposition (CVD), electrodeposition, and electroless chemical reduction. Metallization of polymeric films by these methods involves several stages.²⁴ First, the substrate film is prepared. Second, the surface of the substrate is often modified via plasma, ion beam, electron beam, photolytic, or chemical treatments to enhance metal-substrate adhesion. Third, the metal is deposited onto the film surface. There are serious drawbacks to external deposition for the preparation of metallized polymeric films. First, adhesion of more passive metals, such as silver, gold, copper, etc. to polymers is notoriously poor.²⁵⁻²⁸ Second, external methods are not convenient for preparing films of large area. Third, CVD rarely works well with polymeric films since the film can seldom be heated without degradation or distortion to temperatures needed to effect decomposition of the metal precursor. The limitations of external methods led us to pursue the fabrication of reflective and conductive metallized films utilizing an efficient single-stage in situ chemical reduction process which should be useful for the preparation of continuous films of varied sizes with excellent adhesion at the polymer/metal interface. This procedure can be viewed as the inverse of chemical vapor deposition where an internal rather than an external thermal decomposition/reduction of a polymer-soluble metal complex yields native metal atoms or clusters which diffuse to give an island growth metallized surface.

Experimental Section

Materials. "Ultrapure" 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-oxydianiline (ODA) were obtained from Wakayama Seika Kogyo Co., Ltd. (via Kennedy and Klim, Inc.), and Allco Chemical Corp., respectively. ODA was used as received. BTDA was dried under vacuum at 150 °C for 5 h prior to use; without this drying procedure resins of substantially lower molecular weight are obtained. The melting points of the monomers as determined by differential

(15) (a) Madix, R. J. Oxygen Activation and Oxidation Reactions on Metal Surfaces. In *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E.; Sawyer, D. T., Eds.; Plenum: New York, 1988; pp 253-264 and references therein. (b) R. J. Madix, *Science* **1986**, *233*, 1159.

(16) Gliem, R.; Schlamp, G. Thin Films for Microelectronics. *Metall* **1987**, *41*, 34.

(17) (a) Gierow, P. A. Fabrication of Thin Film Concentrators for Solar Thermal Propulsion Applications. *Proceedings of the ASME-JSME-JSES Solar Energy Conference*, Reno, NV, 1991; pp 1-7. (b) K. Ehrlicke, The Solar Powered Space Ship. ARS paper 310-56, Meeting of the American Rocket Society, Cleveland, OH, June 18-20, 1956.

(18) Gulino, D. A.; Egger, R. A.; Bauholzer, W. F. Oxidation-Resistant Reflective Surfaces for Solar Dynamic Power Generation in Near Earth Orbit. NASA Technical Memorandum 88865, 1986.

(19) Freeland, R. E.; Bilyou, G. In-Step Inflatable Antenna Experiment. 43rd Congress of the International Astronautical Federation, IAF-92-0301, Washington, DC, 1992.

(20) Liedberg, H.; Lundberg, T. *Urol. Res.* **1989**, *17*, 359.

(21) (a) Angelo, R. J. (to Du Pont). Electrically Conductive Polymeric Compositions. U.S. Patent 3,073,785 (Jan 15, 1963). (b) Endrey, A. L. (to Du Pont). Electrically Conductive Polymeric Compositions. U.S. Patent 3,073,784 (Jan. 15, 1963).

(22) Hubin, N.; Noethe, L. *Science* **1993**, *262*, 1390.

(23) Wilbur, J. L.; Jackman, R. J.; Whitesides, G. M.; Cheung, E. L.; Lee, L. K.; Prentiss, M. G. *Chem. Mater.* **1996**, *8*, 1380.

(24) *The Chemistry of Metal CVD*; Kodas, T. T., Hampden-Smith, M. J. Eds.; VCH: Weinheim, 1994.

(25) (a) Gerenser, L. J. *J. Vac. Sci. Technol.*, **A** **1988**, *6*, 2897. (b) **1990**, *8*, 3682. (c) Gerenser, L. J.; Goppert-Berarducci, K. E.; Baetzold, R. C.; Pochan, J. M. *J. Chem. Phys.* **1991**, *95*, 4641. (d) Gerenser, L. J.; Goppert-Berarducci, K. E. *Metallized Plastics*; Mittal, K. L., Ed.; Plenum: New York, 1992; Vol. 3, pp 163-178. (e) Burger, R. W.; Gerenser, L. J. *Metallized Plastics*; Mittal, K. L., Ed.; Plenum: New York, 1992; Vol. 3, pp 179-193.

(26) Mittal, K. L. *J. Vac. Sci. Technol.* **1976**, *13*, 19.

(27) Green, P. F.; Berger, L. L. *Thin Solid Films* **1993**, *224*, 209.

(28) Rozovskis, G.; Vinkevicius, J.; Jaciauskienė, J. *J. Adhes. Sci. Technol.* **1996**, *10*, 399.

thermal analysis were 218 and 188 °C, respectively. DMAc (HPLC grade, <0.03% water), Ag(I) acetate (99.999%), Ag(I) trifluoroacetate (98%), Ag(I) pentafluoropropionate (98%), and Ag(I) heptafluorobutyrate (97%) were purchased from Aldrich Chemical Co. and were used without further purification. Trifluoroacetic acid (Peninsular Chemresearch Inc.) was redistilled under nitrogen.

Film Preparation. The BTDA/ODA poly(amic acid) solution employed in this study was prepared with 1.0 mol % excess of dianhydride at 15% solids (w/w) in DMAc. The resin solution was prepared by first dissolving the diamine⁹ 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 in the range 1.7–1.8 dL/g at 35 °C. In a detailed study²³ on film preparation with BTDA/ODA resins with viscosities from 1.1 to 2.2 dL/g at 35 °C, no large differences in metallized film properties were observed; thus, resin viscosity is not a crucial experimental parameter.

In most instances Ag(I) was introduced into DMAc as the solid crystalline carboxylate salts followed by addition of the BTDA/ODA solution. However, the perfluorocarboxylate salts can be prepared in situ from Ag(I) acetate and the perfluorocarboxylic acid by the following representative procedure. Ag(I) acetate is not soluble in DMAc or a DMAc solution of the BTDA/ODA poly(amic acid). However, if one or more equivalents of a perfluorocarboxylic acid is dissolved in DMAc followed by the addition of Ag(I) acetate, dissolution occurs completely with formation of Ag(I) perfluorocarboxylate salt. Thus, some Ag-containing resins were prepared by first slurrying Ag(I) acetate in a small volume of DMAc (1.5 g of DMAc for every 5 g of 15% BTDA/ODA solution) containing a perfluoroacetic acid. The 15% poly(amic acid) solution was then added by weight to give the final desired concentration. The light yellow Ag-doped resins were stirred thoroughly for 2 h before casting films. Although there is always concern for photochemical decomposition with Ag(I) 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. Doped poly(amic acid) solutions were cast as films onto soft glass plates using a doctor blade set at 15–17 mil to obtain cured films ca. 20–30 μm in thickness. After remaining in an atmosphere of dry (10% relative humidity) flowing air (100 SCFH) for 14–18 h, the tack-free films were thermally cured in a Blue M forced air oven. Details of the thermal cure cycles are given as necessary with the tables presenting film data. Metallic layers formed on both the air side and glass side surfaces during cure. The films were removed from the glass plates by scoring the edges with a razor blade; rarely was it ever necessary to soak the film in deionized water to cause it to release from the plate. Samples for reflectivity measurements were made by casting or affixing films onto 27 × 46 mm glass plates; no differences have ever been observed between films cast and cured directly on glass plates and films mounted on glass plates with double-sided adhesive tape. Reflectivity values reported are the average of four readings taken at different places on the glass slides. These four readings vary ±2%.

Characterization. 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 in sealed pans were determined with a Seiko DSC 210 system with a heating rate of 20 °C/min. Surface resistivities of all films were measured with an Alessi four-point probe. Transmission electron microscopy (TEM) was done on a Zeiss CEM-920 instrument. 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. Atomic force micrographs were done with a Digital Instrument NanoScope III multimode scanning probe microscope.

Results and Discussion

Synthetic Considerations. Representative composite films synthesized from three Ag(I) perfluorocarboxylate complexes, Ag(C_nF_{2n+1}CO₂) *n* = 1, 2, and 3, and BTDA/ODA in DMAc are catalogued in Tables 1, 2, and 3. The films were synthesized by two approaches: (1) casting on a glass substrate and (2) casting on a glass-bound undoped parent BTDA/ODA polyimide base which had been previously thermally cured to the polyimide. Thermal imidization and curing of the poly(amic acid) form of BTDA/ODA containing soluble Ag(I) as a perfluorocarboxylate complex led to polyimide films having metallized surfaces on the air and glass sides of the film. The air-side surfaces exhibit metallic luster and have excellent specular reflectivity and surface conductivity, depending on stoichiometry and the thermal cycle employed. The glass-side surfaces are metallized in an irregular manner; they display minimal reflectivity and are not conductive. The silvered films maintain mechanical properties similar to those of the parent polyimide. This is particularly true for the films of Tables 2 and 3 where a Ag(I)-doped poly(amic acid) film is cured on a polyimide base of BTDA/ODA. Such "film-on-film" specimens are more efficient in the use of Ag and also reduce bubbling which occurs in selected circumstances. All films are flexible and can be creased tightly without breaking. In most cases the films of Tables 1–3 were prepared by dissolving the solid carboxylate complexes in DMAc followed by addition of the poly(amic acid); however, an alternative route is to form the Ag(I) perfluorocarboxylate salt in situ by adding the perfluorocarboxylic acid to a slurry of Ag(I) acetate. The more basic acetate abstracts a proton from the fluorinated carboxylic acid to form the Ag(I) perfluorocarboxylate complex and acetic acid (Scheme 1). This latter approach yields similar results and is convenient when a Ag(I) complex is not easy to prepare and isolate with an available acidic ligand or is difficult to store without decomposition.

Given the ease with which Ag(I) is reduced, $E^\circ = 0.80$ V, a synthetic question arises: Does any Ag(I) compound that is soluble in DMAc and in the solvent free poly(amic acid)-polyimide yield essentially the same metallized surface with respect to reflectivity and conductivity? The answer is no. We have now looked at the metallization efficacy of several soluble compounds including Ag(I) nitrate, Ag(I) tetrafluoroborate, (hexafluoroacetylacetonato)Ag(I), AgHFA, (trifluoroacetylacetonato)Ag(I), AgTFA, (trimethylphosphine)- and (triphenylphosphine)(hexafluoroacetylacetonato)Ag(I), (1,5-cyclooctadiene)(hexafluoroacetylacetonato)Ag(I), Ag(HFA)(COD), and the (trimethylphosphine)iodoAg(I) tetramer. These Ag(I) additives give distinctly different films with regard to reflectivity and conductivity patterns.^{8–12,29} Thus, there is clearly a ligand effect on the polymer-constrained reduction of Ag(I) and subsequent migration to give metallic surfaces. For example, AgHFA prepared in situ gives films with excellent reflectivity (%*R* > 80), but none could be prepared in a conductive state.^{8,9} Simply changing to the trifluoro-

Table 1. Reflectivity, Thermal, Mechanical, Resistivity, and X-ray Data for Silver(I) Perfluoroalkanoate-BTDA/4,4'-ODA Films Cast on a Glass Base^a

entry code	additive (cure cycle) ^d	percent silver (calc) ^b	polymer repeat unit to silver(0) ratio	percent reflectivity of silvered films ^c (as a function of angle)					T _g °C (DSC) and (CTE) (ppm/K)	10% wt loss °C (air)	10% wt loss °C (N ₂)	surface conductivity ^e (polished film) (Ω/N)	X-ray d values (10 ⁻⁸ cm)	tensile strength (Ksi) ^f	percent elongation at break	modulus (Ksi)
				20°	30°	45°	55°	70°								
1	Ag(CF ₃ CO ₂) (100, 200, 300)	9.23	2.18/1	74 (69)	72 (67)	65 (60)	58 (54)	46 (44)	366	561	not conductive (not conductive)	2.40(100), 2.07(34), 1.46(22), 1.24(23)	12.7 (0.49)	10.3 (3.9)	267 (27)	
2	Ag(C ₂ H ₃ O ₂) + CF ₃ COOH (100, 200, 300)	9.30	2.16/1	62 (85)	59 (83)	53 (78)	51 (74)	56 (67)	369	510	not conductive (16)	2.36(100), 2.04(18), 1.44(8), 1.23 (7)	22.0 (0.70)	10.0 (1.3)	473 (27)	
3	Ag(CF ₃ CO ₂) (100, 150, 200, 300)	10.7	1.86/1	65 (97)	59 (93)	52 (91)	46 (87)	45 (78)	377	508	not conductive (19)	2.36(100), 2.04(24), 1.44(13), 1.23(9.7)	22.9 (1.1)	8.6 (1.6)	530 (42)	
4	Ag(CF ₃ CO ₂) (100, 200, 340)	10.6	1.87/1	29 (66)	31 (59)	28 (52)	27 (51)	34 (54)	373	531	not conductive (14)	2.36(100), 2.04(26), 1.45(11), 1.23(9.0)	20.1 (0.50)	9.5 (0.7)	448 (19)	
5	Ag(C ₂ F ₃ CO ₂) (100, 200, 300)	10.2	1.96/1	56 (80)	52 (78)	46 (73)	42 (68)	45 (63)	373	534	not conductive (43)	2.34(100), 2.03(22), 1.45(9.0), 1.23(7.2)	21.0 (0.50)	10.8 (0.7)	444 (19)	
6	Ag(C ₂ F ₃ CO ₂) (100, 200, 340)	10.7	1.86/1	76 (67)	75 (64)	69 (59)	61 (52)	44 (41)	367	558	not conductive (not conductive)	2.35(100), 2.04(31), 1.44(13), 1.23(10)	12.8 (1.1)	15.3 (1.6)	238 (42)	
7	Ag(C ₂ F ₃ CO ₂) (100, 200, 300)	10.7	1.86/1	Both films (7 and 8) are identical in appearance. They are too crinkled and puckered to measure reflectivity although each film is brightly silvered.					274	316	514	not conductive	2.36(100), 2.05(51), 1.64(7.7), 1.44(22), 1.23(20)	mechanical measurements were not possible for these two samples (7 and 8)		
8	Ag(C ₂ F ₃ CO ₂) (100, 150, 200, 300)	10.7	1.86/1						272	365	not conductive	2.33 (100), 2.02(48), 1.44(28)3(27)				

^a The inherent viscosity of the resin in DMAc was 1.7–1.8 dL/g at 35°. The bases were cast from 12% resin solutions at ca. 15–20 mil. Cured film thicknesses were in the 0.75–1.15 mil range.
^b Calculated for the silver(I) perfluoroalkanoate dopant system decomposing completely to silver metal and volatile components which are lost from the film. ^c Reflectivity data are relative to a Perkin-Elmer polished aluminum optical mirror set at 100%—see Experimental Section. The reflectivity values in parentheses are for samples whose surface was polished with a Leblanc model 3292 soft metal polishing cloth. ^d For the 100, 200, 300 °C cure the sample was kept at 100 °C for 1 h, heated to 200 °C over 30 min and held for 1 h, and heated to 300 °C over 30 min and held for 1 h. For the 100, 150, 200, 300 °C cure the sample was kept at 100 °C for 1 h, heated to 150 °C over 30 min and held for 1 h, heated to 200 °C over 30 min and held for 1 h, and heated to 300 °C over 30 min and held for 1 h. For the 100, 200, 340 °C cure the sample was kept at 100 °C for 1 h, heated to 200 °C over 30 min and held for 1 h, and heated to 340 °C over 1 h and held for 1 h. All samples were cooled to ca. 50 °C from their maximum cure temperature over 2 h. ^e Four point probe measurement. ^f Not measurable. ^g The film thickness for the lower tensile strength values of entries 1 and 6 are 1.15 ± 0.1 mil whereas the film thickness for the higher values of entries 2–5 are 0.7 to 0.8 mil.

Table 2. Reflectivity, Resistivity, and X-ray Data for Silver(I) Perfluoroalkanoate–BTDA/4,4'-ODA Films Cast and Thermally Cured on an Imidized Parent BTDA/4,4'-ODA Base^a

entry code	additive	percent silver (calc) ^b	polymer repeat unit to silver(0) ratio	(percent reflectivity of silvered films ^c (as a function of angle))					surface conductivity ^d (polished film) (Ω/\square)	X-ray <i>d</i> values (10^{-8} cm)
				20°	30°	45°	55°	70°		
9	Ag(CF ₃ CO ₂)	10.7	1.86	70 (68)	69 (66)	62 (58)	56 (52)	52 (45)	not conductive (225)	2.36(100), 2.04(31), 1.45(12), 1.23(10)
10	Ag(C ₂ F ₅ CO ₂)	10.6	1.87	56 (65)	53 (63)	49 (60)	45 (58)	47 (58)	not conductive (1050)	2.36(100), 2.14(48), 1.44(25), 1.23(30)
11	Ag(C ₃ F ₇ CO ₂)	10.7	1.85	61 (58)	61 (57)	56 (51)	51 (43)	44 (39)	not conductive (not conductive)	2.35(100), 2.05(46), 1.45(20), 1.23(22)
12	Ag(CF ₃ CO ₂)	4.4	4.84	55 (52)	<i>e</i>	47 (44)	<i>e</i>	36 (37)	not conductive (not conductive)	These four samples (entries 12–15)
13	Ag(CF ₃ CO ₂)	6.3	3.32	53 (52)	<i>e</i>	46 (43)	<i>e</i>	35 (37)	not conductive (not conductive)	show the prominent 111, 200, 220, and
14	Ag(CF ₃ CO ₂)	8.5	2.39	42 (61)	<i>e</i>	39 (54)	<i>e</i>	38 (46)	not conductive (not conductive)	311 Ag° reflections
15	Ag(CF ₃ CO ₂)	10.7	1.86	70 (68)	69 (66)	62 (58)	56 (52)	52 (45)	not conductive (225)	

^a The cure cycle for all films was 100, 200, 340 °C for 1 h each in air with 30 min ramp time to each temperature. The inherent viscosity of the resin in DMAc was 1.7–1.8 dL/g at 35 °C. The bases were cast from 12% resin solutions at ca. 11 mil and when thermally cured had thicknesses of 0.5–0.7 mil. Silver(I)-doped layers were cast on the parent base at ca. 11 mil; the thicknesses of the cured metallized top layer were 0.4–0.7 mil. ^b Calculated for the silver(I) perfluoroalkanoate dopant system decomposing completely to silver metal and volatile components which are lost from the film. ^c Reflectivity data are relative to a Perkin-Elmer polished aluminum mirror set at 100%—see Experimental Section. The reflectivity values in parentheses are for samples whose surface was polished with a Leblanc model 3292 soft metal polishing cloth. ^d Four point probe measurement. ^e Not measured.

acetylacetonate ligand gave films that were only modestly reflective but highly surface conductive.¹² These latter films can be polished to give both high reflectivity ($\%R > 90$) and conductivity; the AgHFA films when polished never give conductive surfaces. Ag(I) nitrate gives brittle films with poor reflectivity ($\%R = 25$).¹⁰ Thus, while not well understood, there are important but subtle ligand effects in tailoring the surface properties of silvered films. Indeed, the present series of Ag(I) perfluoroalkanoate films has a singular and distinctive set of properties relative to films produced with other Ag(I) compounds.

To obtain even modest levels of reflectivity upon thermal reduction, it is essential that the Ag(I) dopant system be soluble in the poly(amic acid)–DMAc solution. The use of insoluble Ag(I) compounds, such as Ag(I) carbonate, Ag(I) oxide, and (2,4-pentanedionato)-Ag(I), gives films in which Ag metal is formed in micrometer-size aggregates, but the reflectivity never exceeds ca. 10%.⁹ A homogeneous mononuclear distribution of Ag(I) in the curing film facilitates the formation of Ag atoms or small clusters which are necessary for migration of Ag to the surface to form the uniform reflective layer. Faupel et al.³⁰ have demonstrated in physical vapor deposition studies with PMDA/ODA (the polyimide formed from pyromellitic dianhydride and 4,4'-oxydianiline) that only atoms or very small clusters of Ag migrate within the polyimide matrix. Indeed, the three Ag(I) perfluorocarboxylate salts used in this study

remain soluble until reduction occurs and lead to metallic surfaces.

The Ag(I)-doped films need to lose solvent in a low humidity film box before thermal curing to prevent bubbling and nonplanarity of the metallized surfaces due to a rapid release of solvent. In general, the cast films were desolvated at room temperature for ca. 18 h in a film box maintained at 10% humidity with 100 SCFH of air flowing. After such a precure treatment there is still ca. 35 wt % solvent in the films (Figure 1). This persistence of DMAc in the resin is consistent with the report of Bower and Frost¹³ who isolated 1:1 crystalline adducts of DMAc with pyromellitic dianhydride and with isophthal(3-aminoanilide); with DMAc and pyromellitic acid a 4:1 adduct was claimed. Curing films at 135 °C for 1 h, as was done for the films of Table 3, does remove virtually all (ca. 99%) the solvent from the film. Solvent removal before thermal metallization keeps the films from bubbling. Bubbling is fostered by the formation of a glass-side metallic surface which adheres poorly to the glass plate and allows even low levels of gaseous effluents to inflate the polymeric film.

We were able to follow the formation of the silvered surface of BTDA/ODA films by casting a doped resin solution onto a set of glass petrographic slides. The slides were cured simultaneously and at selected temperatures individual slides were withdrawn. Figure 2 shows a plot of developing reflectivity as a function of time and cure temperature for a 10.7% Ag resin. After heating at 135 °C for 1 h the Ag(I)-doped films have the same yellow appearance that they had after solvent removal in the film box and the same color as undoped BTDA/ODA films. There were no X-ray diffraction peaks for face-centered cubic (fcc) Ag visible in samples withdrawn from 137 to 202 °C (Figure 3). However, the films withdrawn at 176 and 202 °C had a lustrous metallic surface with reflectivities of 41 and 57%. We interpret the lack of X-ray reflections at 176 and 202 °C as being due to a very thin layer of Ag giving a partially reflective surface and to either minimal Ag(I) reduction in the bulk of the film or Ag(0) particle sizes

(29) (a) Rubira, A. F.; Rancourt, J. D.; Caplan, M. L.; St. Clair, A. K.; Taylor, L. T. *Proc. Am. Chem. Soc., Division of Polymeric Materials: Science and Engineering*, **1994**, *71*, 509. (b) Rubira, A. F.; Rancourt, J. D.; Caplan, M. L.; St. Clair, A. K.; Taylor, L. T. *Chem. Mater.* **1994**, *6*, 2351. (c) Rubira, A. F.; Rancourt, J. D.; Caplan, M. L.; St. Clair, A. K.; Taylor, L. T. *Metal-Containing Polymeric Materials*; Pittman, C. U.; Carraher, C. E.; Culbertson, B. M.; Zeldin, M.; Sheets, J. E., Eds.; Plenum: New York, 1996; pp 357–36.

(30) (a) Faupel, F. Diffusion and Interface Formation at Polymer–Metal Interfaces. *Proc. Int. Conf. Polymer–Solid Interfaces*, Namur, Belgium, Sept. 1991, IOP Publishing: Ltd.: Philadelphia, PA, 1992; p 171. (b) Foltz, A.; Faupel, F. Structural Investigation of the Silver–Polyimide Interface by Cross-Sectional TEM and Ion-Beam Sputtering. *Mater. Res. Soc. Symp. Proc.* **1991**, *203*, 59. (c) Faupel, F. Diffusion of Metals in Polymers. *Defect and Diffusion Forum*, **1993**, *95–98*, 1201.

Table 3. Reflectivity, Resistivity, Mechanical, and Thermal Data for Silver(I) Trifluoroacetate–BTDA/4,4'-ODA Films Cast and Thermally Cured at 135 °C for 1 h/135–300 °C over 4 h/1 h at 300 °C in air^a on an Imidized Parent BTDA/4,4'-ODA Base^b

entry code	additive	percent silver (calc) ^c	polymer repeat unit to silver(0) ratio	percent reflectivity of silvered films ^d (as a function of angle)					T _g °C (DSC) and [CTE (ppm/K)]	10% wt loss °C (air)	10% wt loss °C (N ₂)	surface conductivity ^e (polished film) (Ω/N)	tensile strength (Ksi)	percent elongation at break	modulus (Ksi)
				20°	30°	45°	55°	70°							
16	control	0	∞	not applicable					273	535	not conductive	19.7	16	450	
17	Ag(CF ₃ CO ₂)	6.0	3.46	83 (79)	81 (78)	75 (72)	70 (69)	61 (59)	274	459	not conductive	20.5	14	419	
18	Ag(CF ₃ CO ₂)	10.7	1.85	65 (99)	61 (97)	53 (89)	49 (80)	50 (70)	270	509	not conductive	21.8	11	460	

^a The exact cure cycle is 20 min to 135 °C for 1 h; 4 h from 135–300 °C; 1 h at 300 °C. The inherent viscosity of the resin in DMAc was 1.7–1.8 dL/g at 35 °C. ^b The base was cured with the cycle: 10 min to 100 °C for 1 h; 30 min to 200 °C for 1 h; 30 min to 340 °C for 1 h. ^c Calculated for the silver(I) trifluoroacetate dopant system decomposing completely to silver metal and volatile components which are lost from the film. ^d Reflectivity data are relative to a Perkin-Elmer polished aluminum mirror set at 100%—see Experimental Section. The reflectivity values in parentheses are for samples whose surface was polished with a Leblanc model 3292 soft metal polishing cloth. ^e Four point probe measurement.

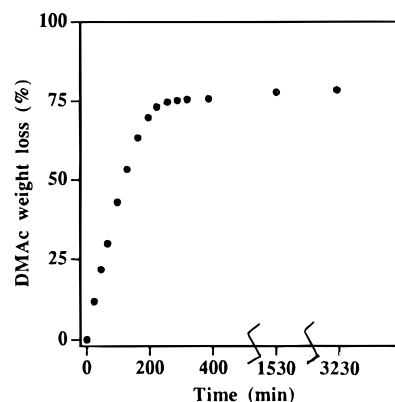


Figure 1. Percent weight loss of dimethylacetamide from a 15.0 wt % BTDA/ODA solution cast at 17 mil on a glass plate and placed in a film box with flowing air at 100 SCFH at 10% humidity.

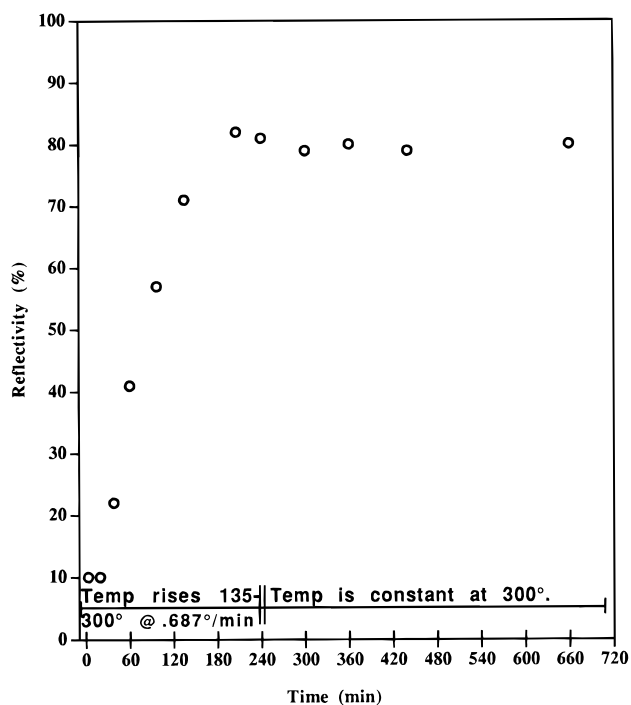


Figure 2. Reflectivity as a function of the thermal cure cycle for a silver-metallized Ag(CF₃CO₂)–BTDA/ODA film with a silver concentration of 10.7%. The film was prepared for 18 h at 23 °C and 10% humidity with flowing air at 100 SCFH. From 135 to 300 °C the temperature rose at 0.685 °C/min; from 240 to 720 min the temperature was constant at 300°. Time zero is at 135 °C.

which are so small that they give undetectable reflections as governed by Scherrer broadening.³¹ We favor a minimal amount of Ag(0) in the bulk of the film rather than very small clusters since at no time in the cure cycle is there any significant reflection broadening.

The development of reflectivity with time and temperature observed for Ag(I) trifluoroacetate is more rapid than that with AgHFA or Ag(HFA)(COD) complexes and much more rapid than that with the AgTFA complex. We suggest that this very rapid reduction may be due to the highly electron-withdrawing nature of the trifluoroacetate ligand, $pK_a = 0.6$, which enhances the

(31) Scherrer, P. *Göttinger Nachrichten* **1918**, 2, 98; Klug, H. P.; Alexander, L. E. *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, 2nd ed.; John Wiley and Sons: New York, 1974.

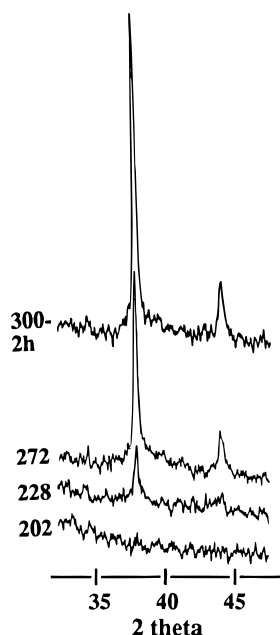


Figure 3. X-ray diffraction patterns in the silver (111) and (200) regions for selected silver-doped films of Figure 2. The temperature at which the film was removed from the cure cycle is at the left of each curve.

tendency of Ag(I) reduction by an external electron donor. This idea is supported by polarographic data on a series of tris(β -diketonato)ruthenium(III) complexes. There is a marked ligand effect on the half-wave potentials with increasingly electron-withdrawing β -diketonate ligands.³² For example, $E_{1/2}$ for the hexafluoroacetylacetonate complex, with hexafluoroacetylacetonate anion being the most electron-withdrawing ligand of the series ($pK_a = 4.35$ for hexafluoroacetylacetonate),³³ is $+0.726$ V; for the trifluoroacetylacetonate complex where the trifluoroacetylacetonate anion is less withdrawing ($pK_a = 6.3$)^{33,34} $E_{1/2}$ is -0.016 V. This demonstrates that ligand effects on oxidation-reduction behavior can be substantial even though there are strong structural similarities. It seems reasonable that the very facile Ag(I) reduction in the Ag(CF₃CO₂) system is due to the electron-withdrawing ability of the fluorinated carboxylate ligand. The development of reflectivity is also more rapid than that obtained with a simple DMAc solvated Ag(I) ion as derived from the dissolution of either Ag(I) nitrate or tetrafluoroborate in DMAc.^{9,10}

We suggest that from 176 to 300 °C there is continual reduction of Ag(I) to the native state coupled with a slow buildup of the surface layer of Ag through migration and sintering effects. From TEM data presented later it is clear that not all of the Ag(0) in the film migrates to the surface. The Ag that resides in the bulk of the polymer after longer cure times does so with larger particle sizes which do not exhibit detectable Scherrer broadening. Residual Ag in the bulk of the film is consistent with observations that only atoms or small clusters migrate into cured PMDA/ODA.³⁰ X-ray reflections are seen near 225 °C, and the intensity of these

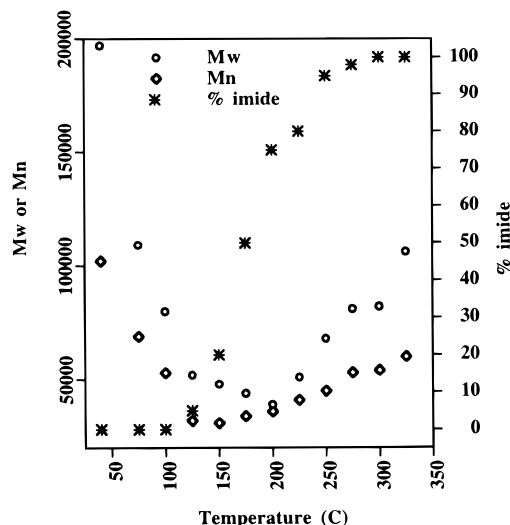


Figure 4. Molecular weight and percent imide formation as a function of temperature in the thermal cure of the poly(amic acid) of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane to the polyimide. M_w , \circ ; M_n , \diamond ; % imide, #.

reflections grows steadily through the final film which was withdrawn from the oven after 7 h at 300 °C. The line width at half-maximum remains essentially constant. This is very different behavior than was observed in previous work with BTDA/ODA and AgTFA, where at cure temperatures up to 300 °C, there was substantial broadening; sharp peaks only appeared after long cure times at 300 °C or heating to 340 °C. If the reduction of Ag(I) occurs early, that is, in the 150–200 °C region, then we might expect there to be facile phase separation of metallic Ag. This is so because in the 125–225 °C region it has been established by Young et al.³⁵ that the molecular weight of a curing poly(amic acid) decreases markedly (Figure 4). This reduced molecular weight is accompanied by a lower viscosity with fewer chain entanglements which means less resistance to Ag atom and cluster migration.

Elemental analysis data are presented in Table 4 for two Ag(CF₃CO₂)-BTDA/ODA films prepared to have 10.7 and 10.6% Ag after thermal curing to 300 and 340 °C, respectively (entries 3 and 4 of Table 1). The elemental percentages found are in reasonable agreement with that expected if Ag(0) is formed and the trifluoroacetate ligand decomposes to volatile compounds which are lost from the system and if Ag in the films does not cause extensive oxidative degradation of the polyimide. The presence of Ag metal, even though it is an organic oxidation catalyst, does not damage the polymer to any great degree.³⁶ There is a small but significant amount of fluorine incorporated into the polymer. Indeed, weak fluorine peaks are seen in the photoelectron spectrum in the C(1s) region at 293 eV and at 589 eV in the F(1s) region, which are fingerprints of the CF₃ group.³⁷ There is no significant difference in the analytical data even though one film was cured to 300 °C and the other film was cured to 340 °C. This

(32) Patterson, G. S.; Holm, R. H. *Inorg. Chem.* **1972**, *11*, 2285.

(33) (a) Jones, J. R.; Patel, S. P. *J. Am. Chem. Soc.* **1973**, *96*, 574.

(b) Taft, R. W.; Cook, E. H. *J. Am. Chem. Soc.* **1959**, *81*, 46.

(34) Reid, J. C.; Calvin, M. *J. Am. Chem. Soc.* **1950**, *72*, 2948.

(35) Young, P. R.; Davis, J. J.; Chang, A. C.; Richardson, J. N. *J. Polym. Sci., Part A* **1990**, *28*, 3107.

(36) (a) Hucknall, D. J. *Selective Oxidation of Hydrocarbons*; Academic Press: London, 1974. (b) Sachtler, W. M. H.; Backx, C.; VanSanten, R. A. *Catal. Rev.* **1981**, *23*, 127.

Table 4. Elemental Analyses for Silver Acetate/Trifluoroacetic Acid-Doped BTDA/4,4'ODA Films

thermal treatment	calculated (wt %)						found (wt %)					
	Ag	F	C	H	N	O ^b	Ag	F	C	H	N	O ^b
100, 200, 300 °C in air	control ^a	0	71.58	2.89	5.72	19.81	0	0.065	70.4	3.05	5.58	20.91
Ag(CF ₃ CO ₂) (entry 3 Table 1)	10.7	0	63.95	2.58	5.11	17.70	9.91	0.79	61.98	2.52	4.81	19.99
Ag(CF ₃ CO ₂) (entry 4, Table 1)	10.6	0	63.99	2.58	5.12	17.70	9.94	0.62	62.38	2.68	5.25	19.13

^a Control is a 1 wt % dianhydride offset. ^b Oxygen values are simply by difference and not by experiment.

is to be contrasted with the use of AgTFA which gave much higher Ag percentages in films cured to 340 °C compared with those cured to only 300 °C. The difference between these two systems is further evidence that the in situ metallization of polymeric films has a strong dependence on the Ag(I) precursor.

Reflectivity, Conductivity, and Surface Characterization. Table 1 displays specular reflectivity data for a series of Ag(I)-doped BTDA/ODA films prepared with Ag(I) trifluoroacetate, pentafluoropropionate, and heptafluorobutyrate and cast directly onto glass plates. Films prepared with Ag(CF₃CO₂) and Ag(C₂F₅CO₂) containing ca. 9 to 11% Ag, when cured to a final temperature of 300 °C, displayed an air-side metallic luster and reflectivities of 42–74%. The variation in reflectivity seems to be associated with the presence of a very faint whiteish “haze” that develops irregularly on film surfaces during the cure. The origin of this haziness is unknown, but it can be removed readily with gentle pressure from a Ag polishing cloth or soft tissue to give much higher reflectivities (entries 2–5 of Table 1). Entry 1 of Table 1 (9.2% Ag) exhibited no haziness. This indicates that the maximum reflectivity that can be developed during the thermal cure alone is ca. 75%. There is no evidence from X-ray diffraction that the “haze” is Ag(I) oxide. This oxide should be thermally decomposed at temperatures ≥ 300 °C. A common problem with the formation of metallic surfaces via chemical vapor deposition using metal complexes with organic ligands is the presence of carbon. For example, in the CVD of Ag on glass, Puddephatt et al.³⁸ found from X-ray photoelectron spectroscopy (XPS) that the surface contained 5–10% carbon. The “haze” may be organic material arising from degradation of metal-enriched polymer surface catalyzed in part by Ag metal. Polishing films cured to 300 °C commonly, but not always, leads to surface conductivity as seen in the Tables 1–3. There seems to be a delicate balance of conditions involved in the formation of the Ag layer. For example, with the 9.2% Ag film mentioned above (entry 1, Table 1), a high level of reflectivity is achieved as the film is taken from the oven. Polishing this film only diminishes the reflectivity, presumably by abrading the surface. Also, polishing this film does not lead to a conductive surface. We attribute this to a very thin polymer overlayer which we have seen regularly with AgHFA–BTDA/ODA films.^{8,9,11} For films prepared with

either Ag(CF₃CO₂) or Ag(C₂F₅CO₂) and cured to 300 °C on glass, there does not seem to be substantial differences in reflectivity and conductivity. However, the Ag(I) heptafluorobutyrate films cured on glass are extensively bubbled to the point where they are useless as reflecting surfaces. These latter films appear metallized, and X-ray diffraction shows fcc Ag. They are not conductive.

Selected films (entries 4 and 6 of Table 1) were cured to 340 °C with the expectation that temperatures greater than 300 °C would give not only high reflectivity but surface conductivity. Higher cure temperatures well above T_g should foster particle mobility and sintering, giving larger Ag particles and enhanced connectivity leading to a conductive surface. However, heating to 340 °C did not give conductive films without physical polishing. As discussed later, moving slowly through the temperature regime of metal ion reduction, 135–300 °C, gives films with optimal properties.

Table 2 contains the results of casting Ag(I)-doped BTDA/ODA films on parent BTDA/ODA base films which were previously cured to 300 °C. (The parent bases were not removed from the glass plate on which they were cured.) The purpose of this was 3-fold. First, this approach is more efficient in the use of Ag since the Ag-doped layer can be cast very thinly on the parent base. Second, the composite films can be tailored to have properties more closely resembling those of the parent polymer since there is very strong adhesion between the parent and Ag-doped polyimide layers.^{8,39} Third, this film-on-film approach greatly reduces the tendency for bubbles to distort the final metallized films as previously discussed. For this film-on-film series, Ag(CF₃CO₂) gives the most reflective film at 70%. This film can be gently polished to give surface conductivity. Ag(C₂F₅CO₂) and Ag(C₃F₇CO₂) give films of lower reflectivity. When cast on a BTDA/ODA base, Ag(C₃F₇CO₂) does not give the bubbling that is seen when cast on glass and yields films with modest reflectivity similar to those of the other two additives. Entries 12–15 of Table 2 show the results of a concentration study (4.4–10.7% Ag) using Ag(I) trifluoroacetate. The highest reflectivity was obtained with a 10.7% film (entry 15), and this was the only film of the series that was conductive with polishing.

Table 3 presents results under the best conditions that we determined for the fabrication of both highly reflective and surface conductive films. For film production with Ag(CF₃CO₂), we found it best to cast a

(37) (a) Wagner, C. D. The NIST X-ray Photoelectron Spectroscopy Database, Technical Note 1289, U.S. Department of Commerce, 1991. (b) *Handbook of X-ray Photoelectron Spectroscopy*; Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E., Eds.; Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, MN.

(38) (a) Yuan, Z.; Dryden, N. H.; Vittal, J. J.; Puddephatt, R. J. *Chem. Mater.* **1995**, *7*, 1696. (b) Dryden, N. H.; Vittal, J. J.; Puddephatt, R. H. *Chem. Mater.* **1993**, *5*, 765.

(39) (a) Brown, H. R.; Yang, A. C. M.; Russell, T. P.; Volksen, W.; Kramer, E. J. *Polymer* **1998**, *29*, 1807. (b) Stoffel, N. C.; Dai, C.; Kramer, E. J.; Russell, T. P.; Deline, V.; Volksen, W.; Wu, W.; Satija, S. *Macromolecules* **1996**, *29*, 6880. (c) Kramer, E. J. *Mater. Res. Soc. Bull.* **1996**, *21*, 37.

Table 5. X-ray Photoelectron Spectroscopy Surface Composition for the Silver Trifluoroacetate-Doped BTDA/4,4'-ODA Films (Relative at. %)

additive/thermal cycle (°C)/sample	percent silver (calc for bulk) ^a	silver ^a	fluorine	carbon	oxygen	nitrogen	surface resistivity (Ω/\square) ^b
AgCF ₃ CO ₂ 100, 200, 340 °C cast on glass. entry 4 of Table 1.	10.6	13.6	0.17	66.4	18.0	1.8	nonconductive
AgCF ₃ CO ₂ 100, 200, 340 °C cast on BTDA/ODA. Entry 9 of Table 2.	10.7	11.3	0.23	66.3	19.1	3.1	nonconductive

^a The Ag 3d photopeaks are very symmetrical and consistent with no significant amounts of silver(I) oxide or fluoride on the surface. These latter two compounds would have peaks 0.5–0.6 eV to the low-energy side of bulk silver metal. ^b These data is consistent with silver(I) acetate–hexafluoroacetylacetone⁹ work which shows that heating to 340 °C does not give conductive films.

Ag(I)-doped BTDA/ODA film on a parent base, which had been cured to 340 °C to ensure complete imidization and removal of volatile materials such as solvent and water. The composite films were allowed to precure in the film box as described earlier. To effect metallization the solvent-depleted composite film was sent through a cure cycle where the temperature increased slowly to 300 °C. Specifically, the thermal cycle involved heating the film in a forced air oven from room temperature to 135 °C over 20 min and holding for 1 h to remove most of the DMAc, heating from 135 to 300 °C over 4 h, and holding at 300 °C for 1 h followed by cooling to 50 °C over 2 h. With these conditions 6.0% Ag films developed reflectivities greater than 80%, but they were not conductive. Polishing 6.0% films did not enhance reflectivity nor render them conductive. When the Ag concentration was increased to 10.7% Ag the reflectivity of the films remained high at 65%; however, when these films were lightly buffed, the reflectivity increased to impressively high values, $R = 95\%$, and these films became conductive. Thus, highly reflective and conductive films can be prepared reproducibly with an economical use of Ag and with thermal and mechanical properties, as presented below, resembling those of the parent polymer.

All the films of Tables 1–3 have strongly adhered surface layers and are completely stable to removal of Ag by a variety of adhesive tapes as per the standard ASTM test. Furthermore, the adhesion of the two polymer layers in the film-on-film samples is outstanding. Soaking or boiling the composite films in water for extended periods of time does not lead to delamination. The mechanism for the strong Ag-polyimide adhesion may be 2-fold. A significant contribution may involve mechanical interlocking. This is supported by XPS surface composition data (Table 5) for the Ag(CF₃CO₂) series of films. The data show that there is only 10–14 at. % Ag on the reflective air-side surface even when the films are cured to 340 °C. Carbon, oxygen, and nitrogen are abundant, which indicates that substantial polymer surrounds and separates the Ag clusters. Adhesion may also be enhanced by the interaction of Ag aggregate surfaces with carboxylate groups. Boerio and co-workers⁴⁰ have concluded from surface-enhanced Raman scattering and XPS of polyimides cured on Ag substrates that imidization is inhibited by the formation of Ag carboxylate complexes by way of the amic acid carboxyl groups. The films studied, however, were cured only to a temperature of 200 °C. Meyer et al.⁴¹

have also reported XPS evidence for the formation of Ag(I) carboxylate complexes with alkylammonium salts of the poly(amic acid) of PMDA/ODA cast on a clean Ag 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 1 h at 300 °C would allow the metal–carboxylate interaction to persist; the poly(amic acid) films of Meyer et al. were only heated to 200 °C. While imidization may be inhibited by the formation of Ag(I) carboxylate complexes, this same interaction may enhance adhesion after thermally curing the polyimide at 300 °C. Indeed, Rubira et al.³⁶ found for metallized BTDA/ODA films formed from Ag(HFA)(COD) that the XPS spectrum had carbon and oxygen photopeaks that matched well with those from Ag(I) benzoate and acetate. Unfortunately, these peaks are not well resolved from other major oxygen photopeaks, and the deconvolution techniques to expose these peaks are open to some question. Finally, Gerenser^{25b} found significantly improved adhesion for Ag 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 Ag(I) carboxylate species in this polyester.

SEM micrographs reveal that the development of Ag clusters at the air-side surface of the polyimide films follows the island growth model.⁴² Figure 5 shows the surface of the 6.0% film of Table 3 (Entry 17) with 83% reflectivity at three magnifications. One sees that there is a regular array of globular Ag. The particle sizes are on the order of 75–100 nm in diameter. TEM micrographs (not displayed) show discrete particles at the surface which are of similar size and which do not form a continuous layer. The microscopy data confirm what is implicit in the XPS and conductivity data; that is, there is a layer of polymer, commingled with metal, at the surface which keeps the Ag particles from contacting one another. The atomic force microscopy (AFM) micrograph (Figure 8) of the 6.0% film exhibits less definition than the SEM, which is consistent with polymer at the surface.

Figure 6 shows a set of SEM micrographs for three of the reflectivity slides prepared in studying the development of reflectivity with time and temperature

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

(42) (a) Ohring, M. *The Materials Science of Thin Films*; Academic Press: New York, 1992; pp 213–219. (b) Venables, J. A.; Spiller, G. D. T.; Hanbuchen, M. Nucleation and Growth of Thin Films *Rep. Prog. Phys.* **1984**, *47*, 399 and references therein.

(40) (a) Young, J. T.; Tsai, W. H.; Boerio, F. J. *Macromolecules* **1992**, *25*, 887. (b) Tsai, W. H.; Cave, N. G.; Boerio, F. J. *Langmuir* **1992**, *8*, 927. (c) Linde, H. G. *J. Appl. Polym. Sci.* **1990**, *40*, 2049.

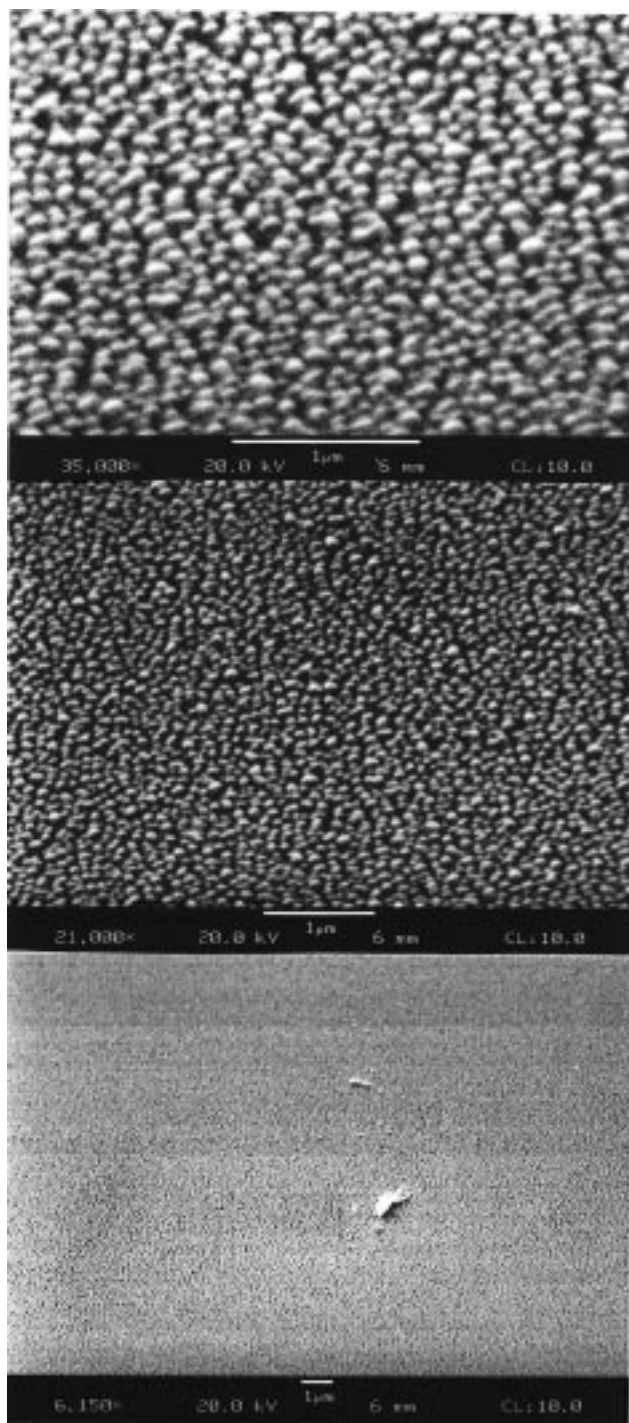


Figure 5. Scanning electron micrographs at different magnifications for the air side of the $\text{Ag}(\text{CF}_3\text{CO}_2)$ -BTDA/ODA film at 6.0% silver cast on a parent BTDA/ODA base (entry 1, Table 3). (Magnifications are indicated on the micrographs with scale bars equal to $1 \mu\text{m}$.)

(Figure 2). The micrographs are for the air-side surface of films withdrawn from the cure oven at 202, 300, and 300 °C after 7 h. Particles emerge gradually over time at the film surface and increase in size with increasing time and temperature. When the film reaches 300 °C, the particle morphology is well established, and a reflectivity of 81% is achieved. The predominate particle sizes are in the range of 100–150 nm. After remaining at 300 °C for 7 h, there is still a preponderance of isolated particles (this film is not conductive); however, the average particle size has increased to 150–

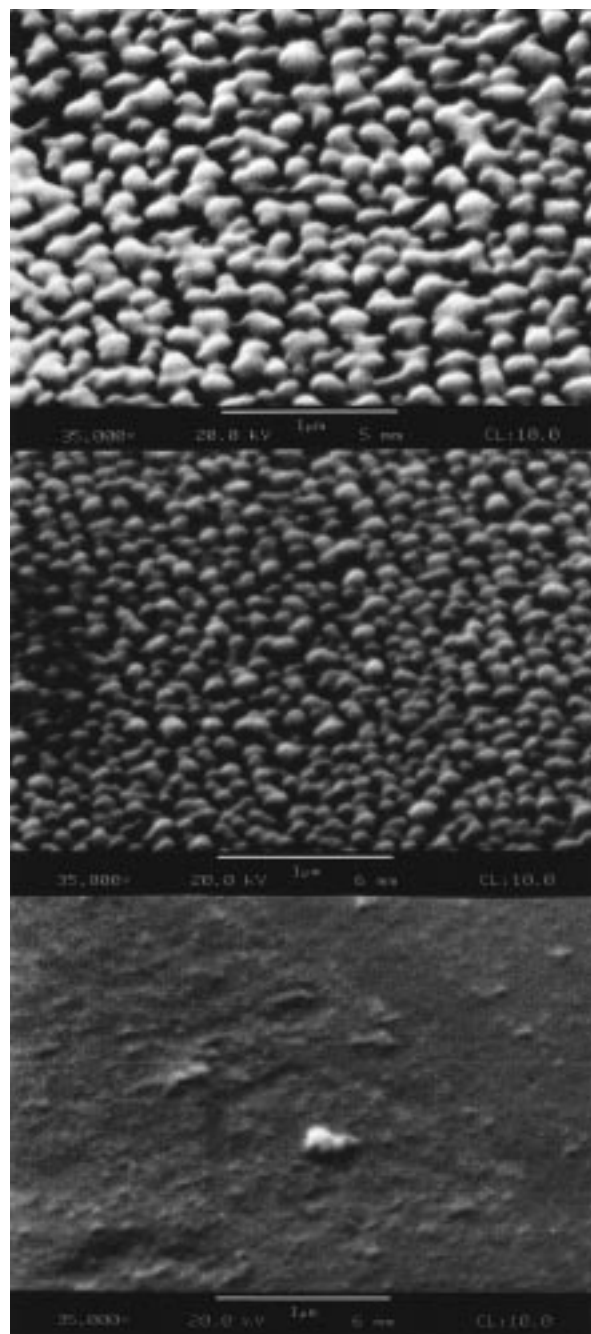


Figure 6. Scanning electron micrographs of the air side for selected samples from the $\text{Ag}(\text{CF}_3\text{CO}_2)$ -BTDA/ODA film series (10.7% silver) that was used to construct the reflectivity vs time-temperature plot of Figure 2. Bottom, reflectivity sample withdrawn from the oven at 202 °C; middle, sample withdrawn at 300 °C; top, sample withdrawn at 300 °C after having been at that temperature for 7 h. (The magnifications are the same for each sample; the scale bar is $1 \mu\text{m}$.)

250 nm. The shapes of the particles after 7 h at 300 °C suggest that there is an increase in size due to sintering and, perhaps, Ostwald ripening. Several apparent "necks" are visible in the micrograph.

The SEM micrographs (Figure 7) show the differences in surface particle morphology that result from heating to a final cure temperature of 300 vs 340 °C. The left side of the Figure 7 shows a 10.7% film (entry 3, Table 1) cured to 300 °C for 1 h. Again, there is evidence of island growth in this nonconducting film. Particle sizes are in the general range of 150–350 nm and appear to

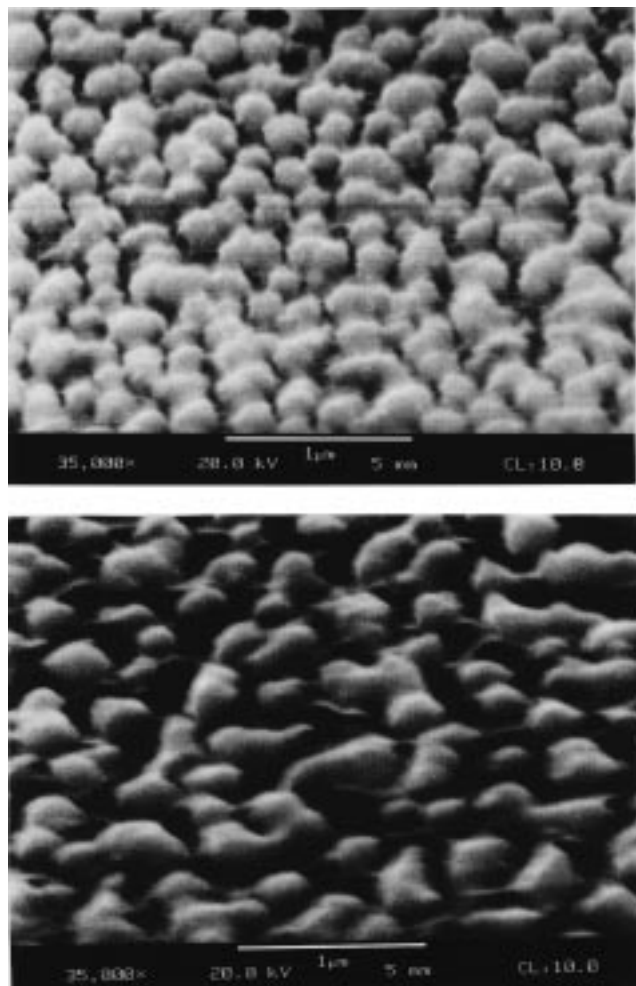


Figure 7. Scanning electron micrographs for the air side of $\text{Ag}(\text{CF}_3\text{CO}_2)\text{-BTDA/ODA}$ films on glass and cured to different final temperatures: left, 10.7% silver film cured to 300 °C (entry 3, Table 1); right, 10.6% silver film cured to 340 °C (entry 4, Table 1). (The magnifications are the same for each sample; the scale bar is 1 μm .)

be insulated from one another by intervening polyimide. For an essentially similar film (10.6% Ag, entry 4, Table 1) cured to 340 °C for 1 h, the right-side micrograph shows that the additional thermal energy causes an increase in particle size with decreasing regularity of form. Again, there is evidence of sintering. The AFM micrograph of the 340 °C film (Figure 8) also shows the presence of large particles which are of irregular size and shape. These SEMs and the AFM for these 10.6 and 10.7% films are different from those for similar films prepared with the AgHFA complex which we reported on earlier.^{8,9} The AgHFA films cured to 300 °C for 1 h show a very regular distribution of isolated Ag islands with particle sizes of ca. 100 nm. For these AgHFA films AFM showed a uniform array of islands but with particle sizes of ca. 200 nm. This size difference may be due to a polymer overlayer which leads to an AFM particle size that is larger than the SEM size, since the SEM emphasizes the contribution of Ag with its greater atomic number to the apparent particle size. Thus, it appears that there is less intervening polymer in the $\text{Ag}(\text{CF}_3\text{CO}_2)\text{-BTDA/ODA}$ system. This is further supported by the fact that heating the AgHFA-BTDA/ODA systems to 340 °C for 1 h never gave a conductive film, nor did polishing these films ever lead to a

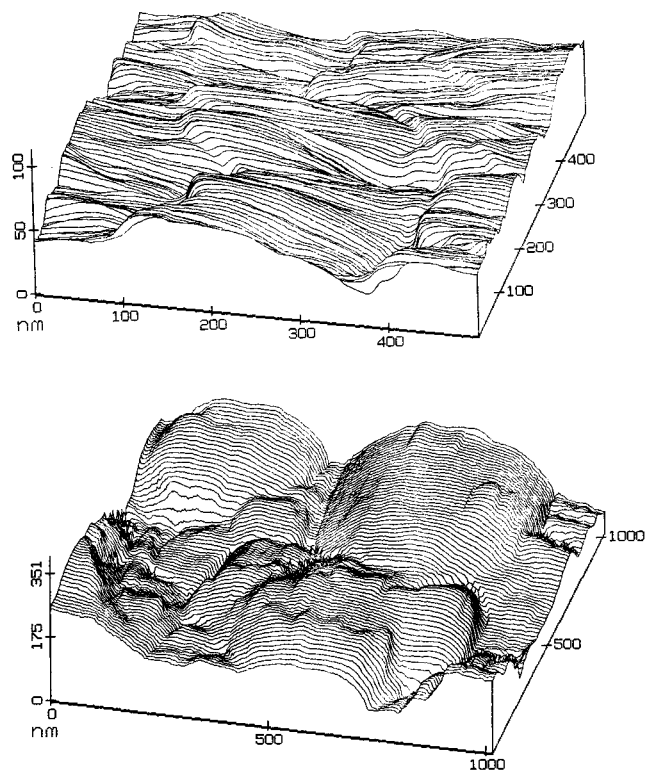


Figure 8. Atomic force micrographs of the air side of $\text{Ag}(\text{CF}_3\text{CO}_2)\text{-BTDA/ODA}$ films: top, 6% silver film cured on a parent BTDA/ODA base (entry 1, Table 3); bottom, 10.7% silver film cured on glass and cured to 340 °C (entry 4, Table 1).

conductive surface. On the other hand, the $\text{Ag}(\text{CF}_3\text{CO}_2)\text{-BTDA/ODA}$ films were commonly made conductive by mild buffing. Apparently, the larger particles in the Ag(I) perfluorocarboxylate systems are more readily mechanically manipulated into electrical contact.

Figure 9 shows a series of TEM micrographs for the 10.7 and 10.6% films (entries 3 and 4 of Table 1) whose SEMs were presented in Figure 7. While the adhesion of the surface layer of Ag is outstanding, some of the ultramicrotomed metallized film sections when set in epoxy lose a portion of the surface Ag particles into the epoxide layer. While this is undesirable to view the entire surface, it is at times beneficial to see individual particles at the surface. If the entire surface layer is intact, there is serious overlapping which makes individual particle visualization difficult. Thus, we chose to display TEMs of a partially delaminated Ag surface. The first feature that one notices is that significant metallization occurs on both the air-side and the glass-side surfaces. Consistent with our earlier work, the glass-side surface is always a very poor reflector and much less regular in particle morphology and distribution. Second, one sees that there is a relatively uniform distribution of small Ag particles in the bulk of the film. We estimate that the particle sizes are ca. 5 nm and larger. This particle size is confirmed by the X-ray patterns which show relatively narrow lines free from Scherrer broadening. For the air side of the film cured to 340 °C, one sees a depletion of Ag particles near the surface. We have observed this depletion with other additives in BTDA/ODA. The origin of this depletion zone has not yet been satisfactorily explained. Third, the TEMs of Figure 9 clearly show that the Ag particle size is larger at both surfaces for the film cured to the

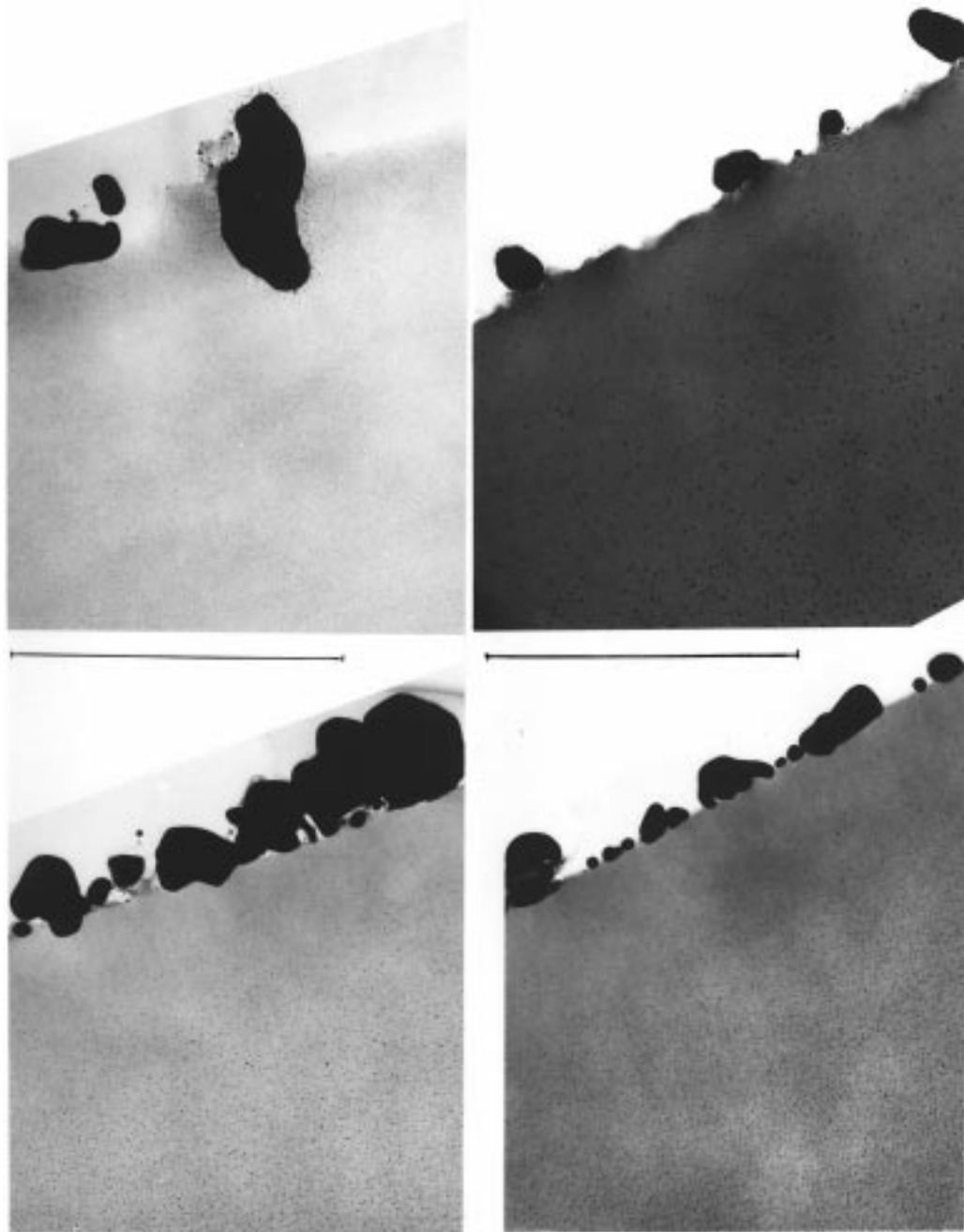


Figure 9. Transmission electron micrographs for $\text{Ag}(\text{CF}_3\text{CO}_2)$ -BTDA/ODA films on glass and cured to different final temperatures: right/top, air side of the 10.7% silver film cured to 300 °C (entry 3, Table 1); right/bottom, glass side of previous film (entry 3, Table 1); left/top, air side of the 10.6% silver film cured to 340 °C (entry 4, Table 1); left/bottom, glass side of previous film (entry 4, Table 1). (The magnifications are the same for each sample; the scale bar is 1 μm .) (See the SEMs of Figure 7.)

higher temperature of 340 °C for 1 h. The sizes (the longest dimension) of the four particles on the air side of the 300 °C film are ca. 85, 160, 170, and 215 nm while sizes for the air side of the 340 °C film are 125, 155, 295, 300, and 590 nm (two of these particles are not shown on the printed micrograph.) Finally, Figure 10 shows a TEM of the 10.7% Ag film cast on a BTDA/ODA base (entry 9, Table 2). A clear separation of the parent base layer and the Ag-doped BTDA/ODA layer is observed. There is no significant migration of Ag into the base layer. This is consistent with rapid formation during the thermal treatment of particles several na-

nometers or greater in size, which are too large to migrate with facility in a polyimide matrix.^{30,43,44}

Thermal and Mechanical Properties. The glass transition temperatures of the metallized films are elevated only slightly (2–6 °C), relative to that of undoped BTDA/ODA, when the metallized films are cured to a final temperature of 300 °C. This suggests that the polymer framework is not compromised to any

(43) Shanker, K.; MacDonald, J. R. *J. Vac. Sci. Technol., A* **1987**, *5*, 2894.

(44) Tromp, R. M.; Legoues, F.; Ho, P. S. *J. Vac. Sci. Technol., A* **1985**, *3*, 782.

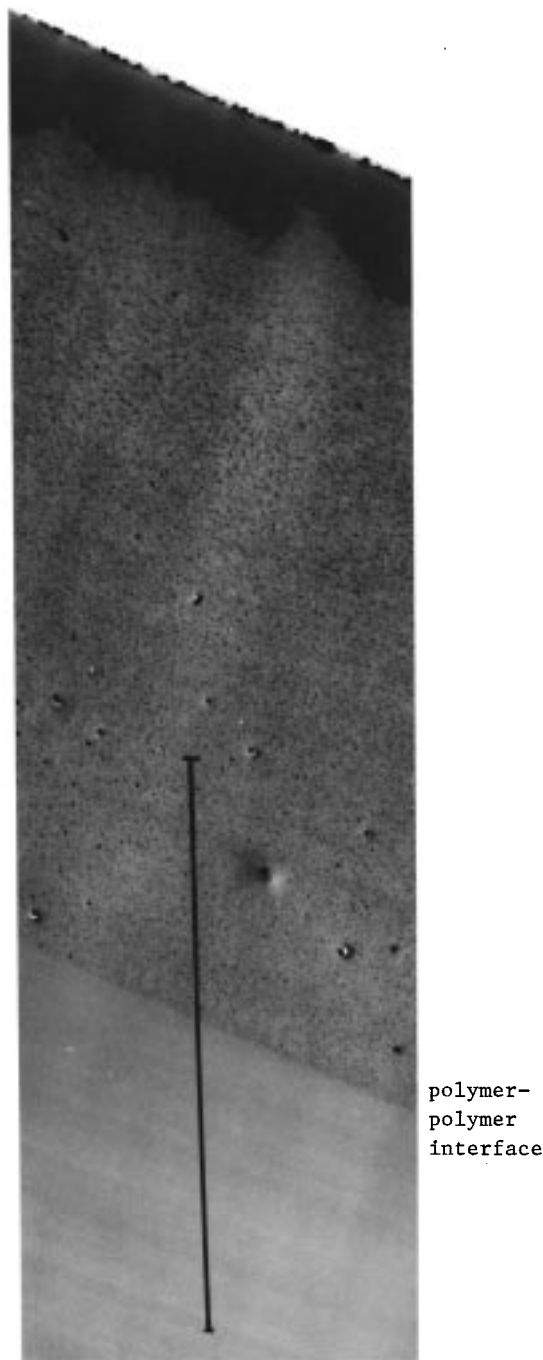


Figure 10. Transmission electron micrograph of the air-side surface and the polymer-polymer interface region for a $\text{Ag}(\text{CF}_3\text{CO}_2)$ -BTDA/ODA film (10.7% silver, entry 9, Table 2) cast on top of a parent BTDA/ODA base. The scale bar is 10 μm .

great degree by the reduction of $\text{Ag}(\text{I})$ and the formation of $\text{Ag}(\text{0})$ which could catalyze polymer oxidation. The similar T_g values are consistent with the passivity of Ag metal toward organic molecules in general and toward the polymer functionalities in particular such that there is no cross-linking of chains via interaction with Ag clusters. However, the formation of metallic Ag clusters in the bulk of the polymer as well as on the surface diminishes the thermal-oxidative stability of the polyimide. While in a nitrogen atmosphere the temperature at which there is 10% weight loss is close to that of the undoped polymer, in air there is a reduction of thermal-oxidative stability with a 10% weight loss

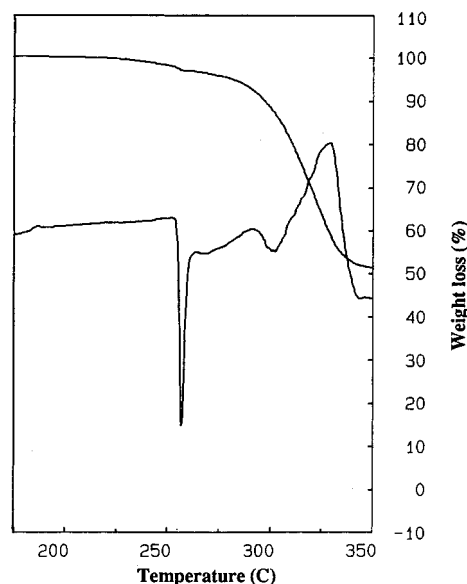
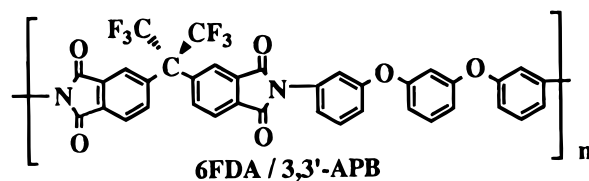


Figure 11. TGA for the thermal decomposition in air of solid silver(I) trifluoroacetate. (Heating rate is 2.5 K/min. The lower trace is the differential thermal analysis curve.)

temperature that is ca. 150 $^{\circ}\text{C}$ lower than the control. Nonetheless, the thermal stability of the mirrored films in air is more than adequate for most purposes.

The mechanical properties for four of the six Ag -doped films cast onto glass are similar to those of the parent undoped film. For one of the $\text{Ag}(\text{CF}_3\text{CO}_2)$ films (entry 1, Table 1) and one of the $\text{Ag}(\text{C}_2\text{F}_5\text{CO}_2)$ films (entry 6, Table 1), the tensile strength and modulus were much lower than the parent. The only difference in these films relative to the other four is that they were 1.15 mil in thickness compared with 0.70–0.80 for the other four films. How this could contribute to lower values is unclear. Nonetheless, all of the films are flexible and have a substantial apparent toughness. The mechanical properties of the film-on-film samples of Table 3 are dominated by the properties of the parent film.

Mechanistic Considerations. $\text{Ag}(\text{I})$ perfluorocarboxylates are all thermally stable solids. Figure 11 displays the TGA curve for $\text{Ag}(\text{CF}_3\text{CO}_2)$. Decomposition to liberate $\text{Ag}(\text{0})$ only begins substantively above ca. 275 $^{\circ}\text{C}$. (The lower curve shows a melting point of ca. 260 $^{\circ}\text{C}$ by DTA.) TGA curves for the other two fluorocarboxylates are similar. From the thermal stability shown by the TGA data we feel that reduction of $\text{Ag}(\text{I})$ in the polymer matrix does not involve the perfluorocarboxylate groups. Water liberated during imidization does not seem to be involved since we found that the soluble polyimide shown below gives a brightly metallized film



when doped with AgHFA in DMAc even though there is no cycloimidization step. In the perfluorocarboxylate systems reasonable sources of the electron for $\text{Ag}(\text{I})$ reduction are the solvent and the polymer. If the electron comes from the polymer, it does so in a manner

which does not do serious damage to the properties associated with the parent polymer. The films of the Tables 1–3 have ca. two polymer repeat units per Ag atom. Thus, if the electron came from the polymer, we might expect to see radical cross-linking and/or polymer damage which should be reflected in T_g . However, large changes T_g are not observed. When $\text{Ag}(\text{CF}_3\text{CO}_2)$ is heated in DMAc without polymer at 135 °C for 15 min, there is reduction of $\text{Ag}(\text{I})$. Thus, residual DMAc could serve as an electron source, particularly if it were coordinated to $\text{Ag}(\text{I})$ in the curing polymer matrix. $\text{Ag}(\text{I})$ –DMAc complexes have been isolated in the solid state and have been demonstrated via NMR. Studies to elucidate the reduction mechanism are in progress.

Conclusions. We have demonstrated that silvered BTDA/ODA polyimide films can be prepared from single-phase homogeneous $\text{Ag}(\text{I})$ perfluorocarboxylate–poly(amic acid) solutions cast on a glass substrate. Depending on concentration and thermal conditions, metallized films can be fabricated with excellent specular reflectivity, surface conductivity, outstanding metal–

polymer adhesion, and the essential mechanical characteristics of the native polyimide. While the formation of metallic Ag lowers thermal film stability in air, the metallized polymers still have a wide thermal use range. $\text{Ag}(\text{I})$ perfluorocarboxylate complexes are readily available in good purity and are thermally and reasonably photochemically stable. The cast films do not have to be protected from light. We have also shown that BTDA/ODA films cast on a parent BTDA/ODA polyimide base yield films with properties similar to those cast on glass. This “film-on-film” approach minimizes the Ag required for the formation of a reflective surface and ensures composite polymer properties which are similar to those of the parent polyimide.

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