

Homogeneous Polyimide Films with Increased Bis(*N,N*-disalicylidene-1,2-phenylenediaminato)zirconium(IV) Content

Liling He, Shawn R. Wagner, and Marvin L. Illingsworth*

Department of Chemistry, Rochester Institute of Technology, Rochester, New York 14623-5603

Andrew J. Jensen

Chemistry, Astra Arcus USA, P.O. Box 20890, Rochester, New York 14602

Glenn P. Yap and Arnold L. Rheingold*

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Received May 12, 1997. Revised Manuscript Received August 14, 1997[⊗]

To increase the concentration of inorganic component in polyimide films and enhance the materials' resistance to atomic oxygen, the complex (4-amino-*N,N*-disalicylidene-1,2-phenylenediaminato)(*N,N*-disalicylidene-1,2-phenylenediaminato)zirconium(IV), Zr(adsp)-(dsp), was synthesized and allowed to react with poly(maleic anhydride) (PMA). The resulting Zr–PMA pendent polymer was mixed with a commercially available polyamic acid of pyromellitic dianhydride and 4,4'-oxydianiline (PMDA–ODA) in various proportions in NMP. Films were then cast onto glass substrates, and thermally imidized. The new mixed ligand complex and the Zr–PMA polymer were characterized by TLC, IR, ¹H NMR, and elemental analysis, along with X-ray crystallography for the former and TGA for the latter. The imidized films of the Zr–PMA polymer blended with PMDA–ODA polyimide were studied by optical examination of multilayer film samples for crack formation, and SEM photography before and after atomic oxygen erosion in a plasma asher. The upper limit of Zr complex incorporation onto prebaked poly(maleic anhydride) was approximately 24% (mol of Zr/mol of repeat units). The upper limit of zirconium complex concentration for the Zr–PMA/PMDA–ODA blends, above which films crack upon imidization, was 8 mol %, compared to 4 mol % for mixtures of Zr(dsp)₂ in PMDA–ODA polyimide.

Introduction

Because of its low density, flexibility, strength, and thermal stability, the polyimide of pyromellitic dianhydride and 4,4'-oxydianiline (PMDA–ODA; Kapton, Dupont) is used to support solar arrays and provide thermal control on a variety of spacecraft. However, it is readily oxidized by atomic oxygen (AO) in low earth orbit (LEO).^{1–3}

Protective films containing a high fraction of metal oxides, such as SiO₂, fluoropolymer-filled SiO₂, and Al₂O₃ films, have been demonstrated in both ground and space tests to be effective in protecting Kapton from oxidation by LEO AO.^{4–6} Such nonvolatile metal oxides, where the oxidation state of the metal matches the

valency of its family in the periodic table, scatter AO upon collision and thus are highly resistant to AO attack.^{4–6} However, although such coatings are themselves AO durable, defects in these coatings do allow AO attack of the underlying Kapton. Undercutting oxidation at defect sites, which typically result from surface irregularities, contaminant particles, abrasion during processing, and/or debris impacts in space, can ultimately lead to complete oxidation of the underlying Kapton if sufficiently high AO exposure occurs.⁴

To avoid the above shortcomings of metal oxide coated Kapton, a modified Kapton designated as AOR (atomic oxygen resistant) Kapton has been proposed as a backup material for the international space station (ISS) solar arrays.⁷ AOR Kapton film is an experimental film made from a blend of polysiloxane–polyimide which is cast from solution and is manufactured by Dupont in a batch process. The polysiloxane component is added to the polyimide to form metal oxide wherever there is AO exposure and thus renders the material less subject to AO damage via surface defect sites. In ground-based

[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1997.

(1) Banks, B. A. Protection of Solar Array Blankets from Attack by Low Earth Orbital Atomic Oxygen ISSN:0160-8371, Proceedings of the 18th Photovoltaic Specialists Conference, Las Vegas, NV, Oct, 1985.

(2) Banks, B. A.; Rutledge, S. K. Low Earth Orbital Atomic Oxygen Simulation for Materials Durability Evaluation. Proceedings of the 4th International Symposium on Spacecraft in the Space Environment, Toulouse, France, Sept 1988.

(3) Leger, L. J.; Visentine, J. T. *J. Spacecr. Rockets* **1986**, *23*, 505–511.

(4) Banks, B. A. SiOx Coatings for Atomic Oxygen Protection of Polyimide Kapton in Low Earth Orbit. Coating Technologies for Aerospace Systems Materials Specialist Conference, Dallas, TX, Apr 1992.

(5) Banks, B. A. Ion Beam Sputter-Deposited Thin Film Coating for the Protection of Spacecraft Polymers in Low Earth Orbit. Aerospace Science Meeting, Reno, NV, Jan 1985.

(6) Rutledge, S. K.; Olle, R. M. Durability Evaluation of Photovoltaic Blanket Materials Exposed on LDEF Tray S1003. The First LDEF Post-Retrieval Symposium, Kissimmee, FL, June 1991.

(7) Rutledge, S. K.; Cooper, J., M.; Olle, R., M. The Effect of Atomic Oxygen on Polysiloxane-Polyimide for Spacecraft Applications in Low Earth Orbit. Space Operations, Applications, and Research Symposium, Albuquerque, NM, June 1990.

plasma ashing tests performed at NASA, AOR Kapton showed a significant improvement in AO resistance over pure Kapton. AOR film weight loss was between 10 and 17% that of unprotected Kapton in a plasma asher.⁷ However, cracking of the material during oxidation caused early structural failure. LEO AO exposure of silicone-containing materials, with synergistic UV effects, can also result in the deposition of a dark contaminant film on adjacent surfaces. Deposition of this type has potential for causing reduced illumination of the solar cells, which will greatly reduce the operating life of spacecraft.^{8,9}

In 1993, tests at the NASA Lewis Research Center showed that a zirconium complex produced no volatile intermediates upon ground-based plasma AO exposure. A sapphire disk located adjacent to a glassy film of the zirconium material bis(*N,N*-disalicylidene-1,2-phenylenediaminato)zirconium(IV), $Zr(dsp)_2$,¹⁰ in an oxygen beam facility upon exposure to a Kapton effective fluence of 8.8×10^{20} atoms/cm² did not show any zirconium upon subsequent examination by X-ray photoelectron spectrometry (XPS) to the instrument's limit of detection (atomic percentage of $\pm 0.1\%$).¹¹

In addition, zirconium complexes were thought to have all other properties required for AOR materials: (a) ZrO_2 has a standard free energy of formation of $\Delta G_f^\circ = -1042.8$ kJ/mol¹² and therefore is one of the most stable metal oxides; (b) organically wrapped Zr should blend better, and thus distribute better, than ZrO_2 in the polyamic acid of Kapton; (c) a ZrO_2 protective layer should form upon AO attack; and (d) more metal oxide will be formed if the protective layer is compromised, i.e., a "self-healing" property similar to that of Si AOR films should be exhibited.

On the basis of these facts and hypotheses, $Zr(dsp)_2$ was mixed with commercially available polyamic acid of PMDA-ODA in 1-methyl-2-pyrrolidinone (NMP), cast onto glass substrates, and imidized. However, when the concentration of $Zr(dsp)_2$ was increased to only 4 mol %, the resulting films became brittle and cracked upon imidization.¹³ Because phase separation is a possible explanation for this phenomenon, we pursued the attachment of zirconium complexes onto a polymer to suppress aggregation of the inorganic phase.

Thus, the synthesis of (4-amino-*N,N*-disalicylidene-1,2-phenylenediaminato)(*N,N*-disalicylidene-1,2-phenylenediaminato)zirconium(IV), $Zr(adsp)(dsp)$, was undertaken¹⁴ (see Figure 1). We now wish to describe the

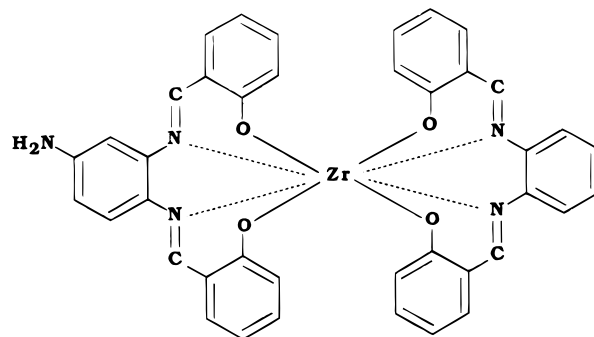


Figure 1. Proposed structural formula for $Zr(adsp)(dsp)$.

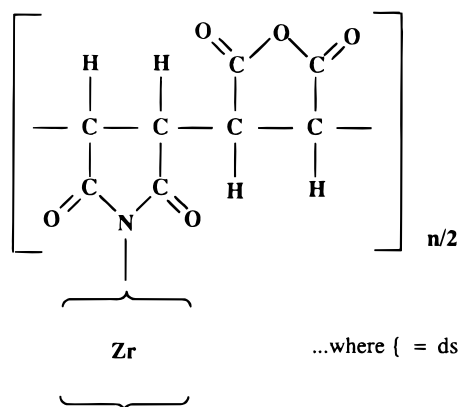


Figure 2. Imidized poly[maleic anhydride- $Zr(adsp)(dsp)$] pendent polymer, a component of the polymer blend with PMDA-ODA polyimide.

reaction of this complex with poly(maleic anhydride) and how the product of this reaction was used to make zirconium-containing PMDA-ODA polyimide blends (see Figure 2). Furthermore, we report the maximum zirconium concentration that could be used in these blends without the films becoming cracked during imidization.

Experimental Section

Preparation of Starting Materials, Pendent Polymer, and Films. Poly(maleic anhydride) (PMA; Polyscience Inc.) was baked at 200 °C for 48 h before use. Analysis of the light brown powder by IR and elemental analysis confirmed its identity as PMA. IR peaks at 1858, 1779 cm⁻¹ are from anhydride (C=O) stretching modes. Calculated for $[C_4H_2O_3]_n$: C, 48.9; H, 2.0; O, 48.9. Found: C, 47.6; H, 3.5; other, 48.8.

(4-Amino-*N,N*-disalicylidene-1,2-phenylenediaminato)(*N,N*-disalicylidene-1,2-phenylenediaminato)zirconium(IV), $Zr(adsp)(dsp)$,¹⁴ The syntheses of the free Schiff base ligands *N,N*-disalicylidene-1,2-phenylenediamine, H_2dsp , and 4-nitro-*N,N*-disalicylidene-1,2-phenylenediamine, H_2ndp , were performed according to published procedures,^{10,15} and their identities verified by melting point and infrared (IR) spectroscopy. Their reaction with zirconium(IV) *n*-butoxide was accomplished by dissolving 12.40 g (39.2 mmol) of H_2dsp and 12.99 g (39.2 mmol) of H_2ndsp in 800 mL of methylene chloride, and then adding, under nitrogen gas, 17.9 mL (39.2 mmol) of 80% $Zr(O-n-Bu)_4$ in *n*-butanol at a rate of 1 drop/2 s. The solution was allowed to stir at room temperature for 10 min and concentrated by rotary evaporation to a volume of 150 mL. The remaining solution was transferred to a Parr bottle, 1 g of 10% Pd on carbon was added, and hydrogenation was conducted at a pressure of 70 psi. After 26 h, thin-layer

(8) Banks, B. A.; Dever, J. A.; Gebauer, L.; Hill, C. M. Atomic Oxygen Interactions with FEP Teflon and Silicones on LDEF. First LDEF Post-Retrieval Symposium, Kissimmee, FL, June 1991.

(9) Banks, B. A.; Rutledge, S. K. The Implication of the LDEF Results on Space Station Freedom Power System Materials. 5th International Symposium on Materials in a Space Environment, Cannes-Mandelieu, France, Sept, 1991.

(10) Archer, R. D.; Day, R. O.; Illingsworth, M. L. *Inorg. Chem.* **1979**, *18*, 4312.

(11) Illingsworth, M. L.; Banks, B. A.; Smith, J. W.; Jayne, D.; Garlick, R. G.; Rutledge, S. K.; de Groh, K. K. *Plasma Chem. Plasma Proc.* **1996**, *16*, 209.

(12) Handbook of Chemistry and Physics, CRC Press: Boca Raton, FL, 75th ed.; 1994-1995; p 5-21.

(13) Illingsworth, M. L.; Wagner, S. R.; He, L.; Betancourt, J. A.; Chen, Y.; Terschak, J. A.; Browning, T. A. Polymeric Materials with Improved Atomic Oxygen Resistance. I. 1994-1995. 6th Annual NASA JOVE Retreat, Monterey, CA, July 1995.

(14) Wagner, S. R.; Illingsworth, M. L. A New Mixed Ligand Bis-(quadridentate)zirconium(IV) Complex for Pendent Polymers. 25th ACS NERM, Rochester, NY, Oct 1995.

(15) Illingsworth, M. L.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 4312.

Table 1. Crystallographic Data for C₄₀H₃₀N₅O₄Zr·CH₂Cl₂.

(a) Crystal Parameters			
formula	C ₄₁ H ₃₂ Cl ₂ N ₅ O ₄ Zr	V, Å ³	3742(1)
formula weight	820.8	Z	4
crystal system	monoclinic	cryst dimens, mm	0.28 × 0.32 × 0.34
space group	P2 ₁ /n	cryst color	dark yellow
a, Å	12.227(2)	D(calc), g cm ⁻³	1.462
b, Å	11.934(2)	(Mo Kα), cm ⁻¹	4.88
c, Å	25.646(9)	temp, K	298
β, deg	90.12(4)		
(b) Data Collection			
diffractometer	Siemens P4	rflns collected	6715
monochromator	graphite	indpt rflns	6560
radiation	Mo Kα (λ = 0.710 73 Å)	indpt obsvd rflns F ₀ > 4σ(F ₀)	4957
2θ scan range, deg	4.0–50.0	std/rfln	3 std/197 rflns
data collected (h, k, l)	+14, +14, +30	var in stds, %	1
(c) Refinement ^a			
R(F), %	6.53	A(ρ), e Å ⁻³	1.3
R(wF), %	10.00	N _o /N _v	12.6
Δσ(max)	0.08	GOF	1.46

^a Quantity minimized = $\sum w\Delta^2$; $R = \sum \Delta / \sum (F_0)$; $R(w) = \sum \Delta w^{1/2} / \sum (F_0 w^{1/2})$, $\Delta = |(F_0 - F_c)|$.

chromatography (TLC) of the hydrogenated solution (10%v/v ethyl acetate–methylene chloride on silica gel) no longer showed the high R_f Zr(ndsp)₂ spot. The solution was then filtered through Celite to remove activated carbon and subjected to rotary evaporation to yield a mixture of three complexes Zr(dsp)₂, Zr(adsp)(dsp), and Zr(adsp)₂. Portions of this mixture were then separated on silica gel (230–400 mesh) columns with 15%(v/v) ethyl acetate–methylene chloride as eluent, and the second bands were consolidated. Hexane was added to this solution, and rotary evaporation was used to induce precipitation. The precipitate was filtered and dried at 100 °C under 1 mmHg vacuum for 3 days to yield the mixed ligand complex Zr(adsp)(dsp). Calculated for C₄₀H₃₀N₅O₄Zr: C, 65.37; H, 3.98; N, 9.53. Found: C, 64.74; H, 4.15; N, 9.34. The minor deviation in %C is attributed to residual solvent in the sample, which is corroborated by the proton nuclear magnetic resonance (¹H NMR) spectrum. A crystal structure was also performed to establish the structure of this complex.

Poly(maleic anhydride-Zr(adsp)(dsp)) Pendent Polymer, Zr–PMA. Poly(maleic anhydride) (0.200 g, 2.04 mmol) and Zr(adsp)(dsp) (0.382 g, 0.51 mmol) were added to a flask with 50 mL of tetrahydrofuran (THF) and stirred at room temperature for about 72 h until no Zr(adsp)(dsp) was detected by TLC (methylene chloride on silica gel). The product was precipitated with hexane, air-dried, and then subjected to Soxhlet extraction with methylene chloride for 48 h until no more yellow color was extracted. The yellow product was then dried under 1 mmHg vacuum at room temperature for at least 3 days, its purity evaluated by TLC (methylene chloride on silica gel), and its composition determined by elemental analysis, FT-IR, and ¹H NMR. Calculated for (C₄₄H₃₁N₅O₇Zr)_n·(C₄H₂O₃)_{3n}: C, 59.7; H, 3.31; N, 6.21. Found: C, 53.3; H, 3.65; N, 5.69.

The solute from Soxhlet extraction was purified chromatographically using the system described above and isolated by rotary evaporation. FT-IR and TLC (70% methylene chloride–30% hexane, silica gel) data were obtained for the isolated solute and compared to those of Zr(dsp)₂ which was synthesized independently.^{10,15}

Preparation of Films of Zr–PMA/PMDA–ODA Polyimide Blends, Zr–PMA/PI. Soxhlet-extracted Zr–PMA polymer was dissolved in dimethylacetamide (DMAc) and mixed with commercially available polyamic acid of PMDA–ODA (Pyralin, Pyre-ML RC5019, Dupont), 15.5% solids in NMP. The mole percentages of Zr in the polymer blends were 4%, 8%, and 10%, respectively. Films were prepared by uniformly spreading the polymer blend solution on glass plates and using a standard imidization procedure, i.e., baking the thin layers of solution at 100, 200, and 300 °C for 1 h each.¹⁶

Instrumental Characterizations. Poly(maleic anhydride) was characterized by thermogravimetric analysis (TGA) on a Seiko TG/DTA220 from 30 to 450 °C at a rate of 10.0 °C/min under nitrogen gas before and after baking at 200 °C for 48 h. Gel permeation chromatography (GPC) was performed with a Unical/Viscotek Model 100 system in THF. Zr(adsp)(dsp) was characterized by IR spectroscopy as KBr mulls over a 4000–400 cm⁻¹ range using a Perkin-Elmer 1760x FTIR, by ¹H NMR spectroscopy in DMSO-*d*₆ with TMS as internal standard using a Bruker WP200 SY FT-NMR, and by X-ray crystallography.

Crystal, data collection, and refinement parameters for the Zr(adsp)(dsp) X-ray crystallography are given in Table 1. A suitable crystal was selected and mounted in a thin-walled, nitrogen-flushed, glass capillary. The unit-cell parameters were obtained by least-squares refinement of the angular settings of 24 reflections (20°–2θ–24°). The systematic absences in the diffraction data are uniquely consistent for space group P2₁/n. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Absorption corrections were ignored ($\mu = 4.88 \text{ cm}^{-1}$). Phenyl rings were refined as idealized rigid bodies. The uncoordinated nitrogen atom was located statistically disordered in two chemically equivalent positions, N(5) and N(5'), with roughly 70/30 distribution. The minor disordered component was refined isotropically. A severely disordered methylene chloride solvent molecule was located and refined isotropically with locked positions. All other non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were ignored. The largest remaining peak in the difference map (1.30 e Å⁻³) occurs at a chemically unreasonable position and was considered to be noise. All software and sources of the scattering factors are contained in the SHELXTL PLUS (4.2) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Soxhlet-extracted Zr–PMA polymer was characterized by TGA on a Seiko TG/DTA220 from 30 to 700 °C at a rate of 10.0 °C/min under air. Single-layer PMA–Zr/PI blend samples which contain 8% by mol of zirconium were examined by SEM before and after 3 h of plasma ashing in a SPI Plasma Prep II asher operated on dioxygen gas. The SEM settings used were a spot size of 200, kV setting of 30 kV, and magnification of 10 000.

Results

Preparation/Characterization of Starting Materials and Zr–PMA. A gradual 23% weight loss is evident in the TGA of a sample of commercial poly(maleic anhydride) over the temperature range 30–200 °C, and a major weight loss event is evident at 312 °C. This gradual weight loss is not observed after baking

(16) *Polyimides: Synthesis, Characterization and Applications*, Mittal, K.L., Ed.; Plenum: New York, 1984; Vol.1.

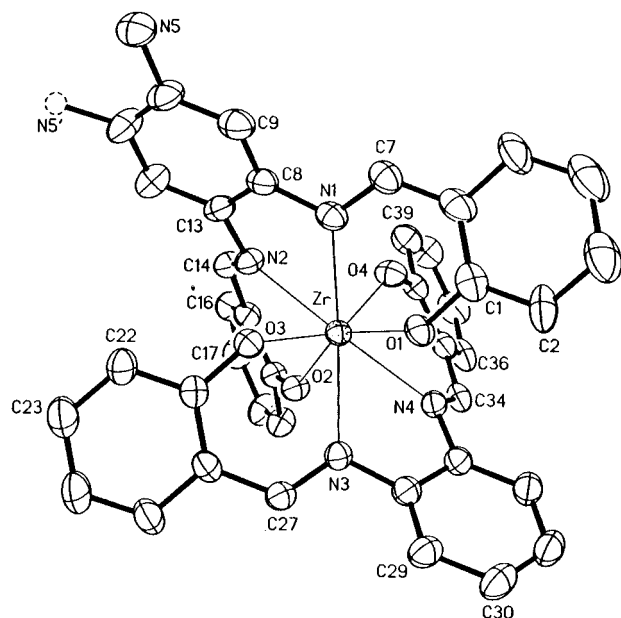


Figure 3. ORTEP of $C_{40}H_{30}N_5O_4ZrCH_2Cl_2$ showing the atomic labeling scheme. Thermal ellipsoids are shown at 35% probability. The minor disordered component of N(5) is rendered in dashed line, and the disordered solvent were omitted for clarity.

at 200 °C for 48 h. GPC results for this batch of commercial poly(maleic anhydride) show that its number average molecular weight is approximately 1980 g/mol and that its polydispersity is 1.09.

For Zr(adsp)(dsp), characteristic FT-IR peaks are observed at 3425, 3350, 1611, and 1311 cm^{-1} and are assigned as primary N-H, (C=N)-Zr, (Ph-O)-Zr stretching, respectively. 1H NMR signals, in ppm downfield from TMS with the corresponding integrations in parentheses, include a singlet at 8.70 (2), two singlets at 8.56 (1) and 8.52 (1), multiplets which range from 7.6–7.45 (4), 7.35–7.23 (5), 7.03–6.86 (4), 6.71–6.68 (2), 6.47–6.38 (4), a doublet at 5.88–5.84 (2), a triplet at 5.76–5.69 (2), and a broad singlet at 5.53 (2). The singlet farthest downfield is assigned to the two imine protons of the dsp(2-) ligand and the two adjacent singlets assigned to the two imine protons of the adsp(2-) ligand based on comparisons to the respective homoleptic complexes Zr(dsp) $_2$ and Zr(adsp) $_2$.^{10,15} The multiplets, doublet and triplet are assigned to the aromatic protons of the coordinated ligands, and the broad singlet is assigned to the amino group protons of the adsp(2-) ligand. The complex does not melt, but shows some discoloration as the temperature approaches 300 °C.

The Johnson's thermal ellipsoid plot (ORTEP) for Zr(adsp)(dsp) is shown in Figure 3, atomic coordinates with estimated standard deviations are included in Table 2, and selected bond lengths and angles are included in Table 3. Selected coordination sphere parameters for Zr(adsp)(dsp), juxtaposed with those for Zr(adsp) $_2$ and Zr(dsp) $_2$, are collected in Table 4 which is included with the Supporting Information.

The reaction of poly(maleic anhydride) and Zr(adsp)(dsp) is slow at room temperature, taking about 3 days to reach equilibrium. The upper limit of complex incorporation was determined to be approximately 25% mol/mol of repeat units. If more than 25% (mol/mol) Zr(adsp)(dsp) is added, the unreacted excess is apparent

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for the Zr(adsp)(dsp) Coordination Sphere

	x	y	z	$U(\text{eq})^a$
Zr	1906.2(4)	2061.7(4)	1009.6(2)	41(1)
O(1)	2479(3)	2343(3)	256(1)	53(1)
O(2)	1630(3)	2756(3)	1742(1)	47(1)
O(3)	248(3)	1924(3)	810(2)	49(1)
O(4)	3320(3)	1286(3)	1281(2)	57(1)
N(1)	1833(4)	303(4)	567(2)	52(2)
N(2)	1204(4)	560(4)	1545(2)	51(2)
N(3)	1242(4)	3928(4)	822(2)	46(1)
N(4)	3292(4)	3534(4)	1074(2)	47(2)
N(5)	-659(7)	-2926(7)	387(3)	75(3)
N(5')	-1499(24)	-2411(26)	1283(10)	96(11)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Lengths (\AA) and Bond Angles (deg) for Zr(adsp)(dsp)

Bond Lengths			
Zr-O(1)	2.080 (4)	Zr-O(2)	2.078 (4)
Zr-O(3)	2.094 (4)	Zr-O(4)	2.077 (4)
Zr-N(1)	2.385 (5)	Zr-N(2)	2.414 (5)
Zr-N(3)	2.417 (5)	Zr-N(4)	2.445 (5)
O(1)-C(1)	1.321 (6)	O(2)-C(20)	1.331 (5)
O(3)-C(21)	1.331 (5)	O(4)-C(40)	1.349 (6)
N(1)-C(7)	1.287 (8)	N(1)-C(8)	1.424 (6)
N(2)-C(13)	1.414 (6)	N(2)-C(14)	1.303 (7)
N(3)-C(27)	1.299 (8)	N(3)-C(28)	1.409 (6)
N(4)-C(33)	1.417 (6)	N(4)-C(34)	1.287 (7)
N(5)-C(10)	1.392 (9)	N(5)-C(11)	1.330 (30)
Bond Angles			
O(1)-Zr-O(2)	145.9(2)	O(1)-Zr-O(3)	96.5(2)
O(2)-Zr-O(3)	95.3(2)	O(1)-Zr-O(4)	95.8(2)
O(2)-Zr-O(4)	90.7(2)	O(3)-Zr-O(4)	148.2(2)
O(1)-Zr-N(1)	73.4(2)	O(2)-Zr-N(1)	140.6(2)
O(3)-Zr-N(1)	77.3(2)	O(4)-Zr-N(1)	78.3(2)
O(1)-Zr-N(2)	140.1(2)	O(2)-Zr-N(2)	74.0(2)
O(3)-Zr-N(2)	74.7(2)	O(4)-Zr-N(2)	77.0(2)
N(1)-Zr-N(2)	66.7(2)	O(1)-Zr-N(3)	77.3(2)
O(2)-Zr-N(3)	76.0(1)	O(3)-Zr-N(3)	72.5(2)
O(4)-Zr-N(3)	139.0(2)	N(1)-Zr-N(3)	134.6(2)
N(2)-Zr-N(3)	132.6(2)	O(1)-Zr-N(4)	73.3(2)
O(2)-Zr-N(4)	76.5(2)	O(3)-Zr-N(4)	137.9(2)
O(4)-Zr-N(4)	73.9(2)	N(1)-Zr-N(4)	133.5(2)
N(2)-Zr-N(4)	137.8(2)	N(3)-Zr-N(4)	65.4(2)
Zr-O(1)-C(1)	135.9(3)	Zr-O(2)-C(20)	137.4(3)
Zr-O(3)-C(21)	132.3(3)	Zr-O(4)-C(40)	134.5(3)
Zr-N(1)-C(7)	126.5(4)	Zr-N(1)-C(8)	115.8(3)
C(7)-N(1)-C(8)	117.5(5)	Zr-N(2)-C(13)	114.9(3)
Zr-N(2)-C(14)	127.8(4)	C(13)-N(2)-C(14)	117.2(5)
Zr-N(3)-C(27)	125.7(4)	Zr-N(3)-C(28)	116.3(3)
C(27)-N(3)-C(28)	117.7(5)	Zr-N(4)-C(33)	114.8(3)
Zr-N(4)-C(34)	126.0(4)		

in the TLC of the reaction solution. For the Soxhlet-extracted and vacuum-dried pure yellow product, characteristic FT-IR peaks due to Zr(dsp) $_2$ groups appear at 1611 and 1311 cm^{-1} and are assigned as indicated above. Peaks due to polymer carbonyl stretching vibrations appear at 1775 and 1709 cm^{-1} , peaks due to carboxylic acid O-H stretching (terminal and bridging) appear at 3650, 3420 cm^{-1} (broad), and a peak due to amide N-H appears at 3250 cm^{-1} (broad). The 1H NMR spectrum in DMSO- d_6 shows broadened signals at 8.7 and 7.8–5.5 ppm assigned to imine and aromatic protons of the complex, respectively. Sharp multiplets centered at 2.2 and 1.8 ppm are assigned to the aliphatic protons of the polymer backbone, and a small broad signal at 8.0 ppm is tentatively assigned as an amide proton.

The elemental analysis results for the Soxhlet-extracted and vacuum-dried yellow product are low in

%C and %N vs those calculated for infinite PMA chains with 25% (mol/mol) Zr pendent groups. From the weakened 1858 and 1779 cm^{-1} IR peaks, this result is due to uptake of water by PMA anhydride groups that remain after the reaction with Zr(adsp)(dsp). Because nitrogen appears only in the zirconium complex, zirconium mole percentage is calculated to be 21–24% (the range based on estimates of water uptake). TGA analysis shows that the decomposition temperature of this material is approximately 280 °C. Upon further heating the TGA residue in air to 700 °C, the zirconium present is converted to the dioxide. From the mass of this residue, the mole percentage of zirconium incorporated into the product is calculated to be 24%, which is in good agreement with the analytical data.

Disproportionation. Formation of a byproduct during the Zr(adsp)(dsp) reaction with PMA was established by TLC results. The byproduct was confirmed to be Zr(dsp)₂ by comparing TLC (50% v/v methylene chloride–hexane on silica gel) and FT-IR data with those of a pure Zr(dsp)₂ sample prepared independently.¹⁰ However, Zr(dsp)₂ was not detected when Zr(adsp)(dsp) alone was subjected to the same conditions used for the Zr–PMA reaction or even when the test was extended for a longer period of time. The mole percentage of pendent groups that disproportionate during the Zr–PMA reaction is determined to be between 3 and 16% depending on the extent of anhydride group hydrolysis assumed; the former value assumes that unreacted anhydride groups remain unchanged and the latter value assumes that anhydride groups are extensively hydrolyzed to carboxylic acid groups during the reaction.

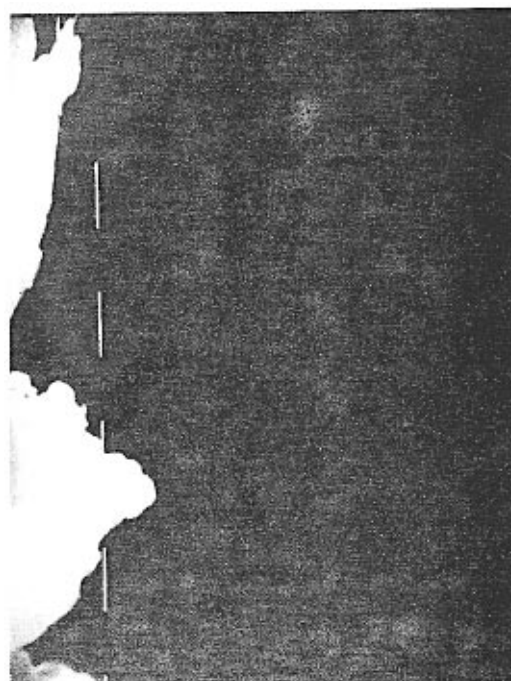
Films of Zr–PMA/PMDA–ODA Polyimide Blends. Films containing 4% and 8% (mol/mol) zirconium complex appear homogeneous and flexible, while film cracking was observed for films containing 10% (mol/mol) zirconium complex.

Figure 4 shows SEM pictures of Zr–PMA/PI films which contain 8% by mole of zirconium before and after 3 h of oxygen plasma ashing. The total atomic oxygen exposure was estimated by comparison to a Kapton standard, and the Kapton effective fluence was found to be approximately 4×10^{20} atoms/cm². Under 10 000 or higher magnification, no phase separation is observed in the film samples before ashing. After 3.0 h of ashing, a wormlike surface topology is observed.

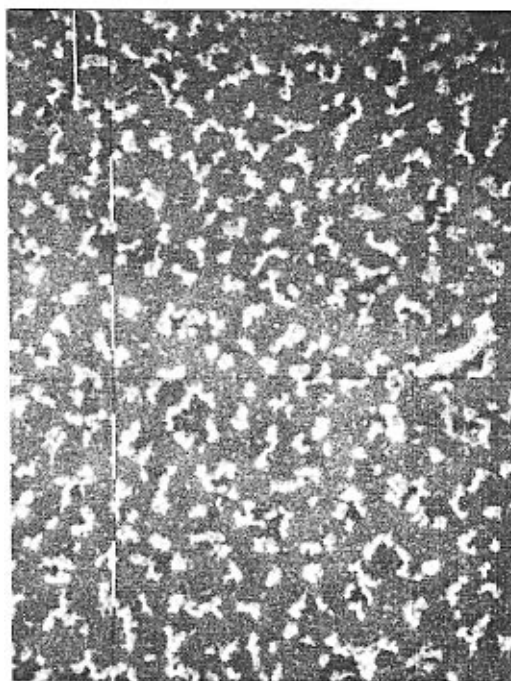
Discussion

Preparation/Characterization of Starting Materials and Zr–PMA. If commercial poly(maleic anhydride) is not subjected to a 48 h baking step, the maximum complex incorporation is only 10% (mol/mol) with additional complex remaining unreacted. In light of the increased incorporation of complex into prebaked polymer, we conclude that many of the polymer's anhydride groups had undergone hydrolysis to carboxylic acid groups, which do not participate in the desired reaction at room temperature. The baking step drives off water, which explains the weight loss from 30 to 200 °C observed by TGA, and enhances the uptake of complex.

Spectral and physical characterizations for Zr(adsp)(dsp) are as expected based on comparisons with those for the homoleptic complexes, with one caveat. The ¹H NMR chemical shifts for the salicylidene ring protons



(a)



(b)

Figure 4. SEM photographs of films of 8% by mole Zr pendent polymer/PMDA–ODA polyimide blends before (a), and after (b), atomic oxygen erosion in a plasma asher.

ortho to the imine bonds appear to be reversed from those in the homoleptic complexes. Specifically, for Zr(adsp)₂ and Zr(dsp)₂, the chemical shifts of these protons are 5.9 ppm (doublet) and 6.0 ppm (doublet of doublets), respectively, whereas for Zr(adsp)(dsp), the upfield signal at 5.9 ppm is the doublet of doublets and the downfield signal at 6.0 ppm is the doublet.

We hypothesize that the electron releasing amino group of the adsp(2–) ligand helps satiate the electron-

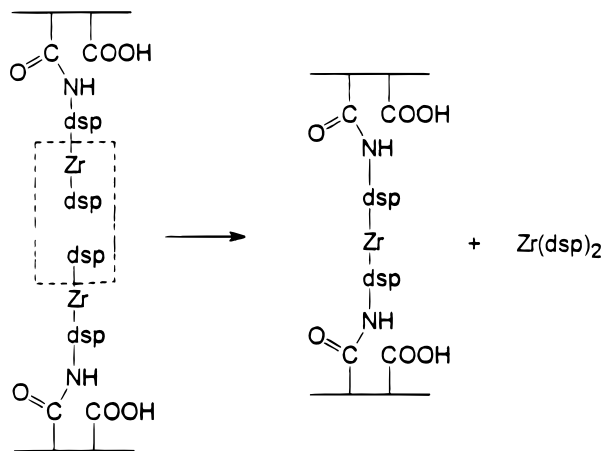


Figure 5. Possible disproportionation mechanism for the Zr pendent groups.

withdrawing zirconium atom.¹⁸ The zirconium, in turn, demands less electron density from the salicylidene rings of the *other* ligand, slightly preserving their ring currents and causing the chemical shifts for the protons in question remain a little farther downfield. More discussion of this hypothesis is included with the Supporting Information.

Upon analysis of the crystal structure of Zr(adsp)-(dsp), including bond lengths, bond angles, and coordination sphere parameters, all values are normal, i.e., within the range of scatter observed for the homoleptic complexes^{10,15} (see Table 4 in the Supporting Information). This scatter presumably arises from crystal packing forces.

The characteristic FT-IR and ¹H NMR peaks of the zirconium complex present in the spectra of the poly(maleic anhydride)-Zr(adsp)(dsp) reaction product, coupled with the absence of free Zr(adsp)(dsp) in its TLC and its yellow color even after Soxhlet extraction, indicate that the complex is bonded to the polymer. The appearance of a ¹H NMR signal which is reasonably assigned to an amide proton supports this conclusion.

The upper limit of Zr complex incorporation was determined to be 24% (mol/mol) from varying reactant ratios and monitoring products with TLC, from elemental analysis data, and from TGA data. The fact that additional Zr(adsp)(dsp) complex over 25% remains unreacted is believed to be due to steric inhibition between Zr complex groups, based on the estimated dimensions of the complexes and of the polymer repeat units.

Disproportionation. Since Zr(dsp)₂ was not detected when pure Zr(adsp)(dsp) was subjected to the same reaction conditions used for the pendent polymer synthesis or even when the test was extended for a longer period of time, the appearance of Zr(dsp)₂ in the appending reaction is not due to the disproportionation of Zr(adsp)(dsp) itself. A possible mechanism by which the disproportionation occurs is shown in Figure 5. We hypothesize that the concentration of complex moieties is higher in proximity to the polymer backbone for Zr-PMA than the concentration of Zr(adsp)(dsp) even in a saturated solution. This locally higher concentration would constitute a stress which, according to Le Chat-

elier's principle, would shift the equilibrium shown in the figure toward the right.

Films of Zr-PMA/PMDA-ODA Polyimide Blends. SEM pictures of PMA/Zr/PI films which contain 8 mol % of complex reveal their homogeneous nature on this scale. Unlike other complexes which aggregate to form clusters upon imidization,¹⁹⁻²² the Zr complex groups must be less mobile in the polymer matrix, more compatible with the polymer structure, or less susceptible to hydrolysis/side reactions during imidization. That is, the Zr complex groups cannot move enough to form detectable aggregates, they gain no thermodynamic advantage by moving, or they can withstand the imidization process better than the complexes used previously and thus remain more compatible. The latter point is plausible in light of the high thermal and hydrolytic stability of Zr(dsp)₂ which are reflected by its decomposition point, 405 °C in air, and the fact that it can be recrystallized from undried solvents.¹⁰ The wormlike erosion is not unlike that for Kapton. As the film surface roughens, increasing surface area accelerates the rate of erosion locally, producing a pitted topology. Erosion of the composite film leaves a white surface residue, however, due primarily to zirconium oxide formation,¹¹ whereas erosion of the Kapton film does not.

As mentioned above, major deterioration of film properties is observed when the concentration of Zr(dsp)₂ in Zr(dsp)₂/PI composites reaches 4 mol %. This limit has been moved up from 4 to 8 mol % of inorganic component by attaching the complex to PMA. We hypothesize that some combination of the following factors contribute to this result. By appending the complex to the polymer, it is possible that the ability of the complex to assume optimum lattice positions is impeded and, thus, phase separation on a scale which is observable by SEM is suppressed. It is also possible that the complex serves as a weak cross-linking agent via dipole-dipole attractions and that free complex is better able to orient itself to perform this function than appended complex. The difference in the extent of this cross-linking would be reflected in the films' properties. By appending functional group derivatives of Zr(adsp)-(dsp) to polymers, which is in progress, the influence of pendent group cross-linking on film properties should be revealed. It is also conceivable that pendent complex groups differ from free complex molecules in the extent to which they interfere with polymer chain entanglement.

In addition to Zr homogeneity and concentration, film thickness is a factor in determining a sample's Zr aerial density and, hence, its stopping power. However, if a uniform zirconium oxide layer is to be generated by AO impacts quickly enough to protect a preponderance of the original material, a homogeneous Zr concentration higher than 8 mol % is needed. Therefore, the appending of Zr(adsp)(dsp) to poly(amic acid) terpolymers to make higher Zr concentration polyimides is also currently in progress.

(19) Nandi, M.; Conklin, J. A.; Salvati, L., Jr.; Sen, A. *Chem. Mater.* **1991**, *3*, 201.

(20) Nandi, M.; Conklin, J. A.; Salvati, L., Jr.; Sen, A. *Chem. Mater.* **1990**, *2*, 772.

(21) Morikawa, A.; Iyoku, Y.; Kakimoto, M.; Imai, Y. *J. Chem. Mater.* **1992**, *2*, 679.

(22) Betancourt, J. A.; Illingsworth, M. L., unpublished results.

(17) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235.

(18) Illingsworth, M. L.; Cleary, B. P.; Jensen, A. J.; Schwartz, L. J.; Rheingold, A. L. *Inorg. Chim. Acta* **1993**, *207*, 147.

Acknowledgment. The authors wish to gratefully acknowledge the NASA Joint Venture program and RIT for financial support of this research. The donation of PMDA–ODA poly(amic acid) in NMP by Dupont, and permission to use a GPC at Lucent Technologies to characterize the poly(maleic anhydride) used in this study, were also very important contributions to this project.

Supporting Information Available: GPC data for poly-(maleic anhydride), additional discussion of Zr(adsp)(dsp)

proton NMR, Table 4 (selected coordination sphere parameters for Zr(adsp)(dsp), with corresponding values for Zr(dsp)₂ and Zr(adsp)₂, and additional crystallographic information for Zr(adsp)(dsp) [Table 2 (complete list of atomic coordinates); list of anisotropic displacement coefficients, and complete lists of bond lengths and angles (11 pages); calculated structure factors (15 pages). Ordering information is given on any current masthead page.

CM970356I