Articles

Oxo-Metal-Polyimide Nanocomposites. 2. Enhancement of Thermal, Mechanical, and Chemical Properties in Soluble Hexafluoroisopropylidine-Based Polyimides via the in Situ Formation of Oxo-Lanthanide(III)-Polyimide Nanocomposites

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Tris(2,4-pentanedionato)lanthanide(III) polyhydrates were added as inorganic sol−gel precursors to DMAc solutions of the polyimides formed from 2,2-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride and 1,3-bis-(aminophenoxy)benzene, 6FDA/1,3(3)-APB and 6FDA/2,2-bis[4-(4-aminophenoxy]hexafluoropropane, 6FDA/4-BDAF. Thermal treatment of doped-resin films gave composite oxo-metal(III) nanocomposite membranes which were visually clear with lower linear coefficients of thermal expansion, increased moduli, and reduced solvent sensitivity. Glass transition temperatures and 10% weight loss temperatures in nitrogen were close to those of the parent polymers. Films were characterized by thermal, mechanical, X-ray, and transmission electron micrographic techniques.

Introduction

The presence of hexafluoroisopropylidene groups, trifluoromethyl groups, and other fluorine-containing segments in high-performance polyimides, relative to traditional nonfluorinated analogues such as Kapton formed from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (4,4′-ODA), leads to several attractive properties including low moisture absorptivity, low dielectric constant, low melt viscosity, resistance to wear and abrasion (i.e., low surface-free energies), low refractive index, and enhanced solubility of the imide form of the polymer in organic solvents.[2] However, uses of many fluorinated polyimides have been limited because of a combination of low glass transition temperatures (Tg), high coefficients of thermal expansion (CTE), low adhesive strength, low tear resistance, high solvent sensitivity, and high cost for all but specialty applications.

Extending earlier patented work[3−5] on the synthesis of the hexafluoro-containing monomers 6FDA, 4-BDAF, and related monomers (Figure 1) and polyimides derived from them, coupled with the insight that meta-substituted diamine monomers decrease intermolecular chain interaction as does the bulky hexafluoroisopropylidene group so that intermolecular charge-transfer complex formation[6,7] is reduced, Jones et al.[8−11] and St. Clair et al.[12−15] reported the synthesis of 6FDA/4-BDAF and

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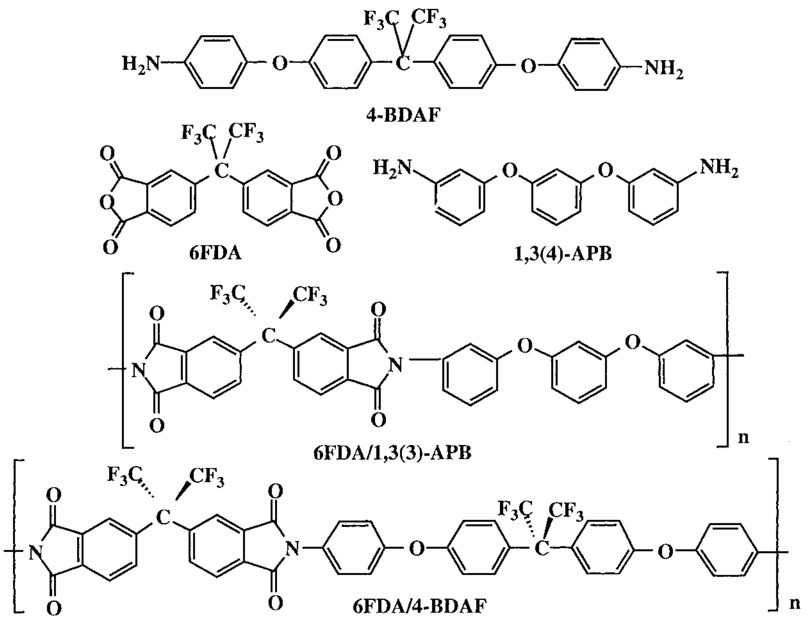

Figure 1. Structures of selected monomers and polymers germane to soluble and colorless polyimides.

Table 1. Thermal, Mechanical, and Solubility Data for Tris(2,4-pentanedionato)holmium(III) Trihydrate-6FDA/1,3(3)-APB Films as a Function of Holmium(III) Concentration[a]

repeat: Ho^{3+} mole ratio	weight % HO_2O_3	CTE (ppm/K)	T_g (°C)	TGA[b] (°C)	tensile strength (MPa)	% elongation[c]	modulus (GPa)	DMAc	diglyme	acetone	$CHCl_3$	MEK
control	zero	49	208	515	121	5.0	3.1	S	S	PS	S	S
10:1	2.6	45	210	482	143	4.4	3.9	PS	PS	PS	PS	PS
7.5:1	3.5	37	209	475	126	4.0	3.8	PS	PS	PS	PS	PS
5.0:1	5.1	33	209	471	134	3.9	4.1	PS	PS	I	PS	PS
2.5:1	9.4	32	210	450	104	2.7	4.3	PS	I	I	PS	I

[a] Films were prepared in DMAc and cured to a final temperature of 300 °C. See Experimental for thermal cure details. [b] The temperature at which there is 10% weight loss. [c] Percent elongation at break.

6FDA/1,3(3)-APB polyimides. These polyimides have excellent transparency in the visible region of the electromagnetic spectrum with ultraviolet cutoffs of ca. 310 nm, low dielectric constants (ca. 2.7), low moisture absorptivity, excellent thermal-oxidative stability, resistance to ultraviolet and 1 MeV electron radiation in nitrogen or in a vacuum, and reasonable mechanical properties. Polyimide films with visible transparency which can endure for long periods in space environments are important for applications involving large-area solar collectors, inflatable antennas, solar arrays, and various space optical devices. However, 6FDA/4-BDAF and 6FDA/1,3(3)-APB have been excluded from many applications because of the marginal properties as mentioned above.

Table 2. Concentration Dependence of CTE for Tris(2,4-pentanedionato)diaquolanthanum(III) and Tris(2,4-pentanedionato)diaquogadolinium(III)-6FDA/1,3(3)-APB Films[a]

repeat:La^{3+} mole ratio[b]	CTE (ppm/K)	repeat:Gd^{3+} mole ratio[b]	CTE (ppm/K)
control (0)	49	control (0)	49
16:1 (1.4)	45.0 44.9 45.0[c]	10:1 (2.5)	41
10:1 (2.3)	43	7.5:1 (3.3)	39
7:1 (3.1)	40	5:1 (4.9)	30
5:1 (4.4)	31	2.5:1 (9.7)	24

[a] The lanthanum(III)-containing films were prepared in a mixed DMAc(45%)-diglyme(55%) solvent; Gd films were prepared in DMAc. All films were cured to a final temperature of 300 °C. See Experimental for thermal cure details. [b] The values in parentheses are the wt % metal(III) oxide based on only Ln_2O_3 remaining in the polyimide after curing. [c] CTE values from three distinct film strips to show measurement reproducibility.

Traditional, that is, nonfluorinated, polyimides usually exhibit CTEs in the range of 30−45 (μm/m)/°C or ppm/K[16,17] and have excellent solvent resistance in the final imide form. Typically, metals and inorganic materials such as silicon, quartz, silicon carbide, alumina, and other metal oxides and ceramics have CTEs in the 0−20 ppm/K range. However, polyimides derived from 6FDA and diamines such as 1,3(3)-APB, 4-BDAF, 4,4′-ODA, *m*-phenylene diamine, 4,4′-6F, and so forth have CTEs of 50−60 ppm/K.[18] Since 6FDA-4-BDAF and 6FDA-1,3(3)-APB are easily prepared from readily commercially available monomers and have several desir-

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Table 3. Thermal, Mechanical, and Solubility Data for Tris(acetylacetonato)Diaquolanthanum(III)-6FDA/1,3(3)-APB at a Polymer Repeat Unit: La^{3+} Molar Ratio of 5:1 as a Function of Cure Cycle[a]

thermal cure cycle	CTE (ppm/K)	T_g (°C)	TGA[c] (°C)	tensile strength (MPa)	% elongation[b]	modulus (GPa)	DMAc	diglyme	acetone	$CHCl_3$	MEK
control 100/200/300	49	208	515	121	5.0	3.1	S	S	PS	S	S
100/150/200/220	41	202	417	115	4.0	3.5	S	PS	I	PS	I
100/150/200/250	33	207	444	105	3.1	3.7	I	I	I	PS	I
100/125/150/175/200/300	31	208	462	112	3.4	3.8	PS	I	I	PS	I
100/150/200/340	34	207	447	106	3.4	3.5	PS	I	I	PS	I

[a] For all cure cycles 30 min was used to move between temperatures listed in column 1. The film sample was held to each temperature for 1 h. Films were prepared in DMAc for thermal and mechancal measurements. [b] Percent elongation at break. [c] The temperature at which there is 10% weight loss.

able properties, we thought it apropos to investigate approaches that would enable the tailoring of CTEs to lower values and decrease solvent sensitivity. The ability to lower CTEs in a controlled fashion is crucial in the fabrication of composite devices, such as integrated circuit broads, to reduce cracking, peeling, warping, and delamination. In this paper, we report research directed at lowering the CTE of 6FDA-4-BDAF and 6FDA-1,3(3)-APB in a controlled manner via the in situ formation of oxo-lanthanide(III)-polyimide nanocomposite materials having low concentrations of the inorganic oxide nanophase. The oxo-metal(III) phases in the hybrid films develop from the hydrolysis and thermal transformation of tris(2,4-pentanedionato)lanthanide(III) hydrate complexes which are initially dissolved with the polyimide in an organic solvent. We also report the effects of oxo-metal(III) formation on other selected thermal, mechanical, and solubility properties and compare these effects where possible with those seen in two-dimensional montmorillonite-polyimide nanocomposites. In Part I of this series[1] it was shown that the CTE of fluorine-containing polyimides is lowered by as much as 30% by the addition of low weight percents of the diaquotris(2,4-pentanedionato)lanthanum(III) complex into solutions of the poly(amic acid) followed by thermal curing to the polyimide.

Experimental Section

Materials. 2,2-Bis(3,4-dicarboxyphenyl)hexafluropropane dianhydride was obtained from Hoechst Celanese and vacuum-dried for 17 h at 110 °C prior to use. 1,3-Bis(3-aminophenoxy)benzene (1,3(3)-APB) was purchased from National Starch and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAF) was purchased from Chriskev; both were used as received. 2,4-Pentanedione, lanthanum(III) oxide, and gadolinium(III) oxide were obtained from Fisher, Aldrich, and Alfa/Aesar, respectively. Tris(2,4-pentanedionato)holmium(III) was purchased from Reacton as an unspecified hydrate. Thermal gravimetric analysis indicated three water molecules per holmium atom which is consistent with early literature and a recent X-ray crystal structure of tris(2,4-pentanedionato)holmium(III) trihydrate by Kooijman et al.[19] showing the structure to be diaquotris(2,4-pentanedionato)holmium(III) monohydrate; we subsequently assumed a trihydrate in the preparation of all films. Holmium(III) acetate tetrahydrate was obtained from Rare Earth Products Limited. Anhydrous holmium(III) acetate was obtained by placing the tetrahydrate under vacuum at 140 °C for 5 h. All other holmium compounds purchased were at a minimum purity of 99.9%. Other tris(2,4-pentanedionato)lanthanum(III) complexes were obtained from Alfa/Aesar and were used as trihydrates. Dimethylacetamide, DMAc, (HPLC grade) and bis(2-methoxyethyl) ether, diglyme, (anhydrous 99.5%) were obtained from Aldrich and were used without further purification.

Preparation of Diqauotris(2,4-pentanedionato)lanthanum(III) and Diaquotris(2,4-pentadionato)gadolinium Monohydrate. Diqauotris(2,4-pentanedionato)lanthanum(III) was made as reported earlier by us[1] following the recipe of Phillips, Sands, and Wagner[20] who verified the structure by single-crystal X-ray analysis. The gadolinium complex was prepared in a manner similar to its lanthanum congener and consistent with the latter procedure of Kooijman et al.[19] who determined the structure to be the same as that for the lanthanum analogue but with molecule of lattice water per gadolinium atom. The resulting crystalline complex was dried at 22 °C in air and used as the trihydrate.

Preparation of the Polyimides. Imidized 6FDA/1,3(3)-APB powder was obtained by the addition of 6FDA (0.5% molar excess) to a DMAc solution of 1,3(3)-APB to first prepare the poly(amic acid) at 15% solids (w/w). The reaction mixture was stirred at the ambient temperature for 7 h. The inherent viscosity of the poly(amic acid) was 1.4 dL/g at 35 °C. This amic acid precursor was chemically imidized at room temperature in an equal molar ratio acetic acid−pyridine solution, the pyridine and acetic acid each being 3 times the moles of diamine monomer. The polyimide was then precipitated in water, washed thoroughly with deionized water, and vacuum-dried at 200 °C for 20 h after which no odor of any solvent was detectable. The inherent viscosity of the polyimide in DMAc was 0.81 dL/g at 35 °C. M_n and M_w were determined to be 86,000 and 289,000 g/mol by GPC, respectively. Imidized 6FDA/4-BDAF powder was prepared similarly with a one-mole percent dianhydride offset. The inherent viscosity of the imide was 1.55 dL/g at 35 °C. GPC gave M_n at 86,000 g/mol and M_w at 268,000 g/mol.

Preparation and Characterization of Oxo-Lanthanum-Polyimide Composite Films. All metal-doped imidized polymer solutions were prepared by first dissolving the metal complex in DMAC and then adding solid imide powder to give a 15% solid (excluding the additives) solution. The solutions were stirred 2−4 h to dissolve all of the polyimide. The clear metal-doped resins were cast as films onto soda lime glass plates using a doctor blade set to give cured films ca. 25 μm in thickness. The films were allowed to sit for 15 h at room temperature in flowing air at 10% humidity. This resulted in a film which was tact free but still had 35% solvent by weight. The films then were cured in a forced-air oven using the thermal cycles indicated in Tables 1−4. For all cure cycles, 30 min was used to move between temperatures at which the samples were held for 1 h. For the films of Tables 2 and 3 terminating at 300 degrees, the cure cycle was 100 for 1 h; 30 min to 125 for 30 min; 30 min to 150 for 30 min; 30 min to 175 for 30 min; 30 to 200 for 30 min; 30 min to 300 for 1 h. For the films of Table 3, the samples 15 min was used in going from 100 to 200 °C; 30 min to 300 for 1 h. The films were removed from the plate by soaking in warm, deionized water.

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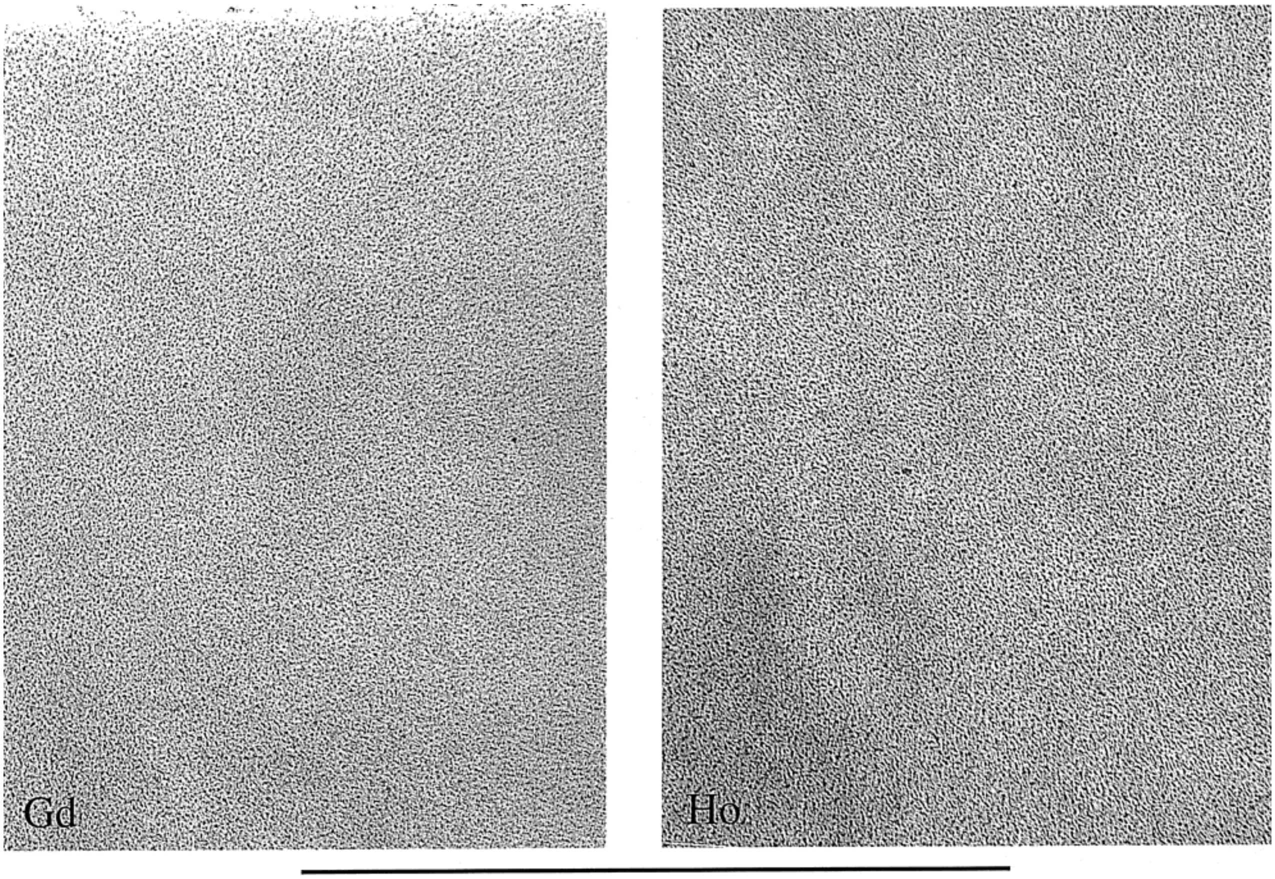

Figure 2. Transmission electron micrographs of the tris(2,4-pentanedionato)gadolinium(III) (left) and tris(2,4-pentanedionato)-holmium(III)-6FDA/1,3(3)-APB (right) films of Tables 1 and 2 at the 5:1 concentration. The scale bar is 1000 nm.

Table 4. CTE and Modulus Data for Tris(2,4-pentanedionato)holmium(III) Trihydrate-6FDA/1,3(3)-APB as a Function of Holmium Concentration Cured to a Final Temperature of 250 °C[a]

repeat: Ho^{3+} mole ratio	weight % HO_2O_3	CTE (ppm/K)	modulus (GPa)
control	0	49	3.1
10:1	2.6	47	3.0
7.5:1	3.5	42	3.0
5.0:1	5.1	27	3.1
2.5:1	9.4	16	3.3

[a] Films were prepared in DMAc. See Experimental for thermal cure details.

Characterization. Solubility studies were carried out by cutting 0.1 g strips of composite polyimide films and placing them in 1 g of solvent. The solvents examined were DMAc, *N*-methylpyrrolidinone (NMP), acetone, ethyl methyl ketone (MEK), chloroform, and diglyme. The solubility and film qualities were visually estimated after 5 days. The films were generally categorized as soluble (S), partially soluble (PS), and insoluble (I). Thermogravimetric analysis (TGA), differential scanning calorimetry, and thermal expansion measurements were performed with Seiko TG/DTA 220, DSC 210, and TMA 100 systems, respectively. TGAs were run under ambient air. Linear coefficients of thermal expansion were determined over a 70−125 °C range. Micrographs were obtained with a Zeiss CEM 902 transmission electron microscope. X-ray data was obtained with a Philips 3600 diffractometer. Mechanical measurements were made at 25 °C on a Sintech Model 2000/2 table top load frame.

Results and Discussion

Film Syntheses. The goal was to prepare composite 6FDA/1,3(3)-APB and 6FDA/4-BDAF films having a uniformly dispersed nanometer-sized lanthanum(III) oxide phase. The expectation was that the inorganic particles, formed via hydrolysis and thermal transformation of tris(2,4-pentanedionato)lanthanide(III) hydrate complexes, would result in a tailored lowering of the linear CTE without compromising other essential polymer properties and would preserve the visual clarity of the films via formation as nanometer-sized grains. Films were typically prepared at a molar concentration ratio of polymer repeat unit to lanthanide(III) ion of ca. 5:1; concentrations lanthanide(III) greater than ca. 2.5:1, particularly for 6FDA/1,3(3)-APB films, generally gave films which fractured on folding tightly. The composite (oxo-lanthanide)-polyimide films were prepared by dissolving the tris(2,4-pentanedionato)lanthanide(III) hydrates (i.e., eight-coordinate diaquotris-(2,4-pentanedionato)lanthanide(III) complexes based on the known crystal structures[19,20] of the lanthanum(III) and gadolinium(III) complexes) in dimethylacetamide (DMAc) followed by addition of the soluble imidized form of 6FDA/1,3(3)-APB or 6FDA/4-BDAF. The films were most often heated to 300 °C and remained transparent throughout all stages of thermal treatment. The transmission electron micrographs (Figure 2) for 5:1 Gd(III) and Ho(III)-6FDA/1,3(3)-APB films of Tables 1 and 2 indicate the presence of oxo-metal particles which are only a few nanometers in diameter. The X-ray diffraction pattern (Figure 3) for the 5:1 tris(2,4-pentanedionato)holmium(III)-6FDA/APB film of Table 1 suggests that the oxo-metal(III) phase is not crystalline; only an amorphous halo for the polyimide is seen. The presence of oxo-metal species in the thermally cured films

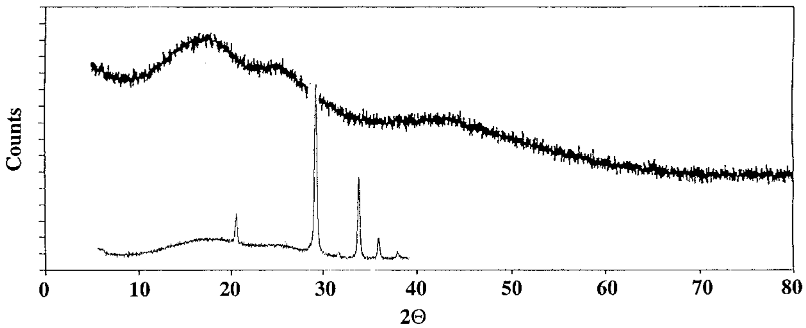

Figure 3. X-ray diffraction patterns for the 5:1 tris(2,4-pentanedionato)holmium(III)-6FDA/1,3(3)-APB film of Table 1 (top trace) and the 5:1 holmium(III). Oxide-6FDA/1,3(3)-APB film (bottom trace) where holmium(III) oxide was added as a pure finely ground insoluble powder. (Counts axis—arbitrary units.)

Table 5. CTE and Modulus Data for Tris(2,4-pentanedionato)holmium(III) Trihydrate-6FDA/1,3(3)-APB as a Function of Holmium Concentration Cured to a Final Temperature of 220 °C[a]

repeat: Ho^{3+} mole ratio	weight % HO_2O_3	CTE (ppm/K)	modulus (GPa)
control	0	49	3.1
10:1	2.6	47	3.0
7.5:1	3.5	49	3.1
5.0:1	5.1	41	3.2
2.5:1	9.4	23	3.3

[a] Films were prepared in DMAc. See Experimental for thermal cure details.

Table 6. Thermal and Mechanical Data for 6FDA/1,3(3)-APB Composite Films Formed with Selected Tris(2,4-pentanedionato)lanthanide(III) Complexes, Tris(2,4-pentanedionato)aluminum(III), and Tetrakis(2,4-pentanedionato)zirconium(IV)[a]

metal 2,4-pentanedionate additive	CTE (ppm/K)	T_g (°C)	TGA[b] (°C)	tensile strength (MPa)	% elongation	modulus (GPa)
none	49	207	515	123	5.1	3.1
$La(acac)_3$	31	209	430	113	3.4	3.8
$Sm(acac)_3$	35	212	477	97	3.2	3.4
$Eu(acac)_3$	36	212	461	112	3.6	3.6
$Gd(acac)_3$	30	210	456	104	3.3	3.5
$Ho(acac)_3$	33	210	468	136	4.0	4.1
$Er(acac)_3$	32	210	464	119	4.2	3.4
$Tm(acac)_3$	32	210	482	108	3.7	3.4
$Al(acac)_3$	44	210	513	117	4.5	3.2
$Zr(acac)_4$	45	210	511	110	3.7	3.4

[a] Films were prepared in DMAc at the 5:1 repeat-to-metal ratio and cured to a final temperature of 300 °C. See Experimental for thermal cure details. [b] The temperature at which there is 10% weight loss.

Table 7. Thermal and Mechanical Data for 6FDA/4-BDAF Composite Films Formed with Selected Tris(2,4-pentanedionato)lanthanide(III) Complexes and Tris(2,4-pentanedionato)aluminum(III)[a]

metal 2,4-pentanedionate additive	CTE (ppm/K)	T_g (°C)	TGA[b] (°C)	tensile strength (MPa)	% elongation	modulus (GPa)
none	51	266	515	93	6.1	2.3
$La(acac)_3$	39 (29)[c]	274	561	105	9.2	2.2
$Gd(acac)_3$	35	271	473	106	10.8	2.6
$Ho(acac)_3$	37	270	478	100	6.6	2.6
$Tm(acac)_3$	38	271	489	103	9.6	2.1
$Al(acac)_3$	45	268	500	104	7.7	2.4

[a] Films were prepared in DMAc at the 5:1 repeat-to-metal ratio and cured to a final temperature of 300 °C. See Experimental for thermal cure details. [b] The temperature at which there is 10% weight loss. [c] CTE value of 29 ppm/K is at a polymer repeat-unit-to-metal(III) ratio of 3.9:1 or 4.3 wt % La_2O_3.

increases the adhesion of the film to the glass casting plate. Thus, it was often necessary to soak the composite films in 70 °C water to obtain free-standing films ca. 25 μm thick. The lanthanide(III)-2,4-pentanedionate complexes investigated with 6FDA/1,3(3)-APB and 4-BDAF were those of La, Sm, Eu, Gd, Ho, Er, and Tm; additionally, tris(2,4-pentanedionato)aluminum(III) and tetrakis(2,4-pentanedionato)zirconium(IV) were studied. Tables 1–7 display synthetic and characterization details for the films of this study.

Film Properties: Linear Coefficients of Thermal Expansion. Table 1 presents data as a function of concentration for tris(2,4-pentanedionato)holmium(III) trihydrate-6FDA/1,3(3)-APB films prepared from DMAc solutions and heated to 300 °C. The CTE of the undoped parent film is 49 ppm/K. The CTE decreases from 49 to 33 ppm/K as the concentration of an oxo-holmium(III) phase (formed from the thermally promoted hydrolysis/transformation of the tris(β-diketonate) complex) decreases from a polyimide repeat unit to metal ion ratio of 10:1 (2.6 wt % Ho_2O_3) to 2.5 (9.4 wt % Ho_2O_3). If pure, insoluble, microcrystalline Ho_2O_3 powder is added to a DMAc solution of 6FDA/1,3(3)-APB, opaque films are produced showing no reduction in CTE. CTE data for additional films prepared from diaquotris(2,4-pentanedionato)lanthanum(III) and diaquotris(2,4-pentanedionato)gadolinium(III) are shown in Table 2. For these latter two systems, there is a similar CTE lowering. While the gadolinium(III) system gives a very low CTE at the 2.5:1 concentration, these films are less flexible and fracture on creasing tightly. At 5:1 or lower concentrations, the Ho, La, and Gd complexes give similar CTE lowerings while retaining the flexibility of the parent film. Figure 4 displays graphically the CTE trends for the Ho, La, and Gd-based 6FDA/1,3(3)-APB films. The curves were generated by an exponential fit with r^2 values of 0.79, 0.95, and 0.96, respectively.

Intense interest exists in preparing polymer composites containing low weight percentages (<10%) of two-dimensional delaminated nanometer-sized montmorillonite silicate sheets. Such composites have enhanced moduli, reduced gas permeability, higher heat distortion temperatures, and lowered CTEs. Included in Figure 4 is CTE data for montmorillonite-PMDA/4,4′-ODA films studied by Yano et al.[21] The similarity among the lanthanide(III) and montmorillonite systems suggests preliminarily that the quasi-spherical nanometer-sized

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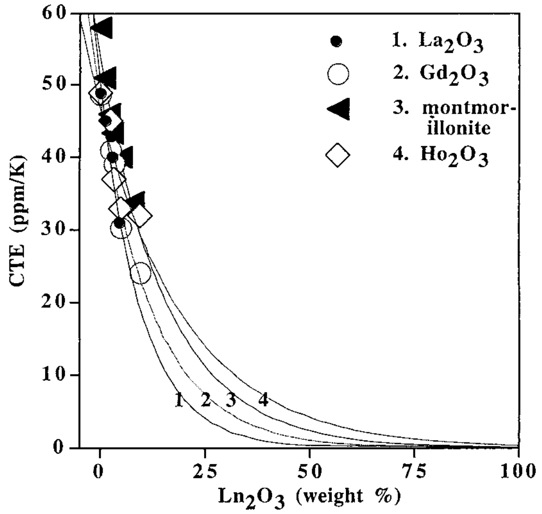

Figure 4. Linear coefficient of thermal expansion versus lanthanide(III) oxide concentration. The lanthanide(III) species are in 6FDA/1,3(3)-APB; the montmorillonite is in PMDA4,4′-/ODA. (Curves are an exponential fit with r^2 for curves 1−4 being 0.90, 0.95, 0.79, and 0.96, respectively).

oxo-lanthanide(III) particles may influence physical properties in a manner similar to that of the clay sheets. That is, the effects on polymer properties may be related predominately to high effective surface areas of small particles regardless of shape.

One concern is whether any randomly chosen lanthanide(III) complex, soluble in the polyimide-DMAc solution, would give similar CTE lowerings. That is, is there anything singular about the 2,4-pentanedionate-lanthanide(III) systems? We have previously synthesized 6FDA/3,3′-APB composite films using five tris(1,3-diphenyl-1,3-propanedionato)lanthanide(III) (Ce, Eu, Gd, Er, and Tm) complexes[22] and five additional lanthanide(III) acetate tetrahydrates (Dy, Er, Tm, Yb, and Y) as additives.[23] With films cured at temperatures of 300 °C, the tris(1,3-diphenyl-1,3-propanedionato)-complexes (Ce, Eu, Gd, Er, and Tm) gave an average CTE lowering of only 1 ppm/K, and the tris(acetato) tetrahydrates (Dy, Ho, Er, Tm, Yb, and Y) gave an average lowering of only 3 ppm/K. In no case was the 1,3-diphenyl-1,3-propanedionato-complex lowering greater than 2 ppm/K and the acetate-complex lowering greater than 5 ppm/K. Furthermore, we have examined several lanthanide(III) complexes with hexafluoroacetylacetonate, trifluoroacetylacetonate, and trifluoroacetate ligands. These complexes give a combination of bubbled, brittle, and seriously discolored films. Thus, it appears that the chemistry involved with the lanthanide(III)-2,4-pentanedionate hydrates in forming an inorganic-polyimide hybrid material may be rather distinctive.

Table 3 shows the CTE dependence for diqauotris-(2,4-pentanedionato)lanthanum(III)-6FDA/1,3(3)-APB films at the 5:1 concentration as a function of four different final cure temperatures, 340, 300, 250, and 220 °C. Since the composite polyimide films are prepared from the fully imidized form of the polymer, it is not necessary to heat the films to 300 °C to ring close the amic acid sites. However, it does require relatively high temperatures for effective solvent removal. The CTE lowerings shown in Table 3 are similar to those observed for the holmium(III) analogues of Tables 1, 4, and 5. That is, heating to a final temperature of 250 °C or higher gives large and similar CTE lowerings. Heating to 220 °C still lowers CTE values but less than heating above 250 °C.

Table 6 shows CTE data for several additional tris-(2,4-pentanedionato)lanthanide(III)-6FDA/1,3(3)-APB films prepared in DMAc. Apparently, all lanthanide-(III) complexes lead to significant and approximately similar CTE lowerings at the 5:1 concentration. This raises the question as to whether nonlanthanide(III) 2,4-pentanedionate metal complexes would give similar composite film properties. To address this query, we prepared and characterized 6FDA/1,3(3)-APB films formed with tris(2,4-pentanedionato)aluminum(III) and tetrakis(2,4-pentanedionato)zirconium(IV). These latter two additives gave only minimal CTE lowerings suggesting again that there is some unique chemistry attributable to the lanthanide-2,4-pentanedionate complexes. Bergmeister and Taylor[24] found that tris(2,4-pentanedionato)iron(III) when added to the poly(amic acids) of BTDA/4,4′-ODA and PMDA/4,4-ODA and thermally cured gave dark brown to black films "some [of which] were flexible; however, all the films fractured when creased." (CTEs were not measured.) Thus, in the formation of hybrid films, there does appear to be singular chemistry involved with $[Ln(acac)_3(H_2O)_2]$ complexes that is not general to all 2,4-pentanedionate-metal complexes.

Table 7 displays data for four tris(2,4-pentanedionato)lanthanide(III) complexes and tris(2,4-pentanedionato)aluminum(III) in 6FDA/4-BDAF films at 5:1. 6FDA/4-BDAF has a lower CTE, modulus, and tensile strength than 6FDA/1,3(3)-APB but a significantly higher glass transition temperature, 266 versus 207 °C. The CTE values for the 4-BDAF films with lanthanide additives are lower than that of the parent film, but the reductions in CTEs are not as great as for the analogous 5:1 1,3(3)-APB films. However, when the 6FDA/4-BDAF films are adjusted so that the final metal(III) oxide weight percent is the same as that for the 1,3(3)-APB analogues, the CTE values are lowered similarly. This can be seen from data for 6FDA/4-BDAF where at a 5:1 repeat unit to lanthanum(III) ratio or 3.4 wt % La_2O_3 the CTE is 39 ppm/K (versus 51 ppm/K for the parent film), whereas when the repeat unit to lanthanum(III) is raised to 3.9:1 or 4.3 wt % La_2O_3, the CTE is lowered to 29 ppm/K. This is to be compared with the 6FDA/1,3(3)-APB lowering from 49 to 31 ppm/K at 4.4 wt % La_2O_3.

Film Properties: Thermal, Mechanical, and Solubility Properties. Consistent with observations presented in Part I[1] of this series, the change in the glass transition temperatures for the 6FDA/1,3(3)-APB samples is minimal at only 2−5 °C. For the 6FDA/4-BDAF samples (Table 7), T_g is modestly elevated from 2 to 8 °C. Since T_g values for the nanocomposite films cured

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to 250 and 300 °C are similar to those for the parent polyimide, cross-linking interactions must be weak. Such weak interactions would be consistent with the fact that the amide and phenyl ether donors are only weak Lewis bases. David and Scherer[25] found that a nanometer-sized SiO_2 phase generated by controlled hydrolysis of tetraethoxysilane in poly(ethyloxazoline) gave virtually no change in T_g of the polymer up to 20 wt % SiO_2, and Leezenberg and Frank[26] found that the in situ precipitation of SiO_2 at 20−30 wt % in poly(diemthylsiloxane) "does not affect the T_g". Thus, with the low weight percents of metal(III) used in our work and the minimal changes in T_g with silicon-oxo phases, it is not surprising that the lanthanide(III)-hybrid films of this work show no dramatic changes in T_g. The essential constancy of T_g values also suggests that there are no metal(III) Lewis acid-catalyzed covalent (C−C, C−O, or C−N) cross-linking reactions between chains, which would be expected to increase T_g dramatically as for polystryene, cross-linked with para-divinylbenzene cross-linking.[27]

The temperature at which there is 10% weight loss in air decreases regularly with increasing metal concentration as can be seen in Table 1 for the tris(2,4-pentanedionato)holmium(III)-6FDA/APB series. However, at a concentration of 5:1 the polyimide composites still have excellent thermal stability. The aluminum(III) and zirconium(IV) β-diketonate complexes give films with minimal CTE lowering and also give only modest change in the temperature at which there is 10% weight loss in air.

For the series of holmium(III)-β-diketonate films of Table 1, there is an increase in modulus relative to the parent film of ca. 30% even at the lowest holmium concentration of 10:1. The tensile strength increases slightly for the films from 10:1 to 5:1. For most of the lanthanide(III)-2,4-pentanedionate films of this study which were cured to a final temperature of 300 °C, the modulus increases. However, for the series of tris(2,4-pentanedionato)holmium(III)-6FDA/1,3(3)-APB films cured to lower final temperatures of 250 and 220 °C (Tables 4 and 5), the modulus did not vary significantly with the oxo-holmium(III) concentration from 10:1 to 5:1; even at the 2.5:1 concentration there was only a modest increase in modulus. Tensile strengths for the composite films varied with no apparent trends. All of the films in the concentration range 10:1 to 5:1 were flexible and could be tightly creased without fracture.

When one looks at the effect of montmorillonite clay sheets on the mechanical properties of PMDA/4,4′-ODA as reported by Tyan et al.,[28] there is a notable increase in modulus with increasing silicate concentration. This is displayed graphically in Figure 5. When the modulus versus metal(III) oxide concentration for the holmium(III) films of Table 1 is plotted with the montmorillonite data, it is apparent that the response for both systems is similar. Given the correspondence of CTE and modulus behavior between holmium(III) and montmorillonite-polyimide systems, it seems appropriate to suggest that highly dispersed quasi-spherical nanometer-sized metal oxide particles in polymer matrixes may give effects similar to two-dimensional silicate sheets.

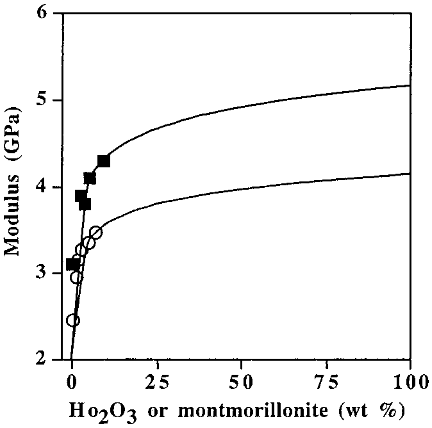

Figure 5. Tensile modulus versus weight percent of inorganic oxide. Holmium(III) oxide formed from tris(2,4-pentanedionato)holmium(III) in 6FDA/1,3(3)-APB (top curve) and organically modified montmorillonite silicate sheets in PDA/4,4′-ODA (bottom curve). Curves were drawn by a logarithmic fit; $r^2 =$ 0.84 and 0.99, respectively.

While fluorinated polyimides are often soluble in the imide form which increase processing options, final products of these polymers remain susceptible to distortion, property modification, and failure because of their continued solvent sensitivity. Thus, we investigated the solubility of selected composite films of this study. As seen from Tables 1 and 3, formation of oxo-lanthanide nanocomposite film leads to a qualitative increase in solvent resistant. To our knowledge, no one has reported the effect of silicate sheets on polyimide solubility.

Rationale for the Use of Lanthanide(III)-Based Inorganic Phases. We chose to investigate lanthanide(III) ions because they exhibit a single, stable tervalent oxidation state with crystal radii from 117 to 100 pm, La(III) through Lu(III).[29] The large radii lead to high coordination numbers for lanthanide complexes with eight being most common.[30−37] Thus, in the lanthanide series one has metal ion additives for polymers which have enlarged coordination spheres and which are hard Lewis acids. These two effects enhance binding of polymer donor atoms, particularly the weakly basic oxygen atoms as they might occur in imide or ether moieties of 6FDA/1,3(3)-APB and 6FDA/4-BDAF. Such metal−polymer coordination, or "site isolation" as christened by Sen et al.,[38,39] has been suggested as the basis for the formation of a homogeneous distribution of

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nanometer-sized oxo-metal clusters throughout a polymer matrix.[38−42]

Metal alkoxides have been widely used in the generation of inorganic−organic hybrid materials, particularly for the formation of silica, titania, and zirconia phases. The use of mixed alkoxo-2,4-pentanedionato-metal complexes has been reported to moderate the hydrolytic activity of alkoxides and to give rise to smaller oxo-metal cluster sizes in polymers.[43−45] Metal complexes without alkoxide but only 2,4-pentanedionate ligands are generally hydrolytically stable under neutral conditions; hence, these complexes have not found significant use in forming oxo-metal nanocomposites. However, diqauotris(2,4-pentanedionato)lanthanum(III), while air stable at 25 °C, becomes a glassy plastic solid when heated over the temperature range 80−95 °C.[46] As reported in Part I,[1] TGA data show the loss of both 2,4-pentanedione and water before 100 °C is reached. McLain[47] has shown that this loss of water and 2,4-pentanedione results in the tetranuclear lanthanum(III)-2,4-pentanedionate complex, $[La_4(O)(C_5H_7O_2)_{10}]$, with a tetrahedral $La_4(\mu_{4-}O)$ core where a single oxygen atom is at the center of a tetrahedron defined by lanthanum(III) ions. Thus, we postulate that with $[La_4(O)(C_5H_7O_2)_{10}]$ formed from diqauotris(2,4-pentanedionato)lanthanum(III) and other lanthanide(III)-2,4-pentanedionate hydrate complexes, there might be a facile route to an initial oxo-metal phase in a heated polyimide matrix. This unique chemistry observed with diaquotris(2,4-pentanedionato)lanthanide(III) complexes may explain why other β-diketonate complexes do not give high quality composite films with lowered CTEs as discussed earlier. For example, the tris(1,3-diphenyl-1,3-propanedionato)lanthanide(III) complexes do not occur as hydrates and are exceptionally thermally stable.

Conclusions. The dissolution of the eight-coordinate diaquotris(2,4-pentanedionato)-lanthanide(III) complex species in DMAc and diglyme (data not shown) solutions of the soluble polyimides 6FDA/1,3(3)-APB and 6FDA/4-BDAF gave thermally cured films with linear coefficients of thermal expansion lowered to a maximum of ca. 40% while maintaining essential mechanical and thermal properties and visual clarity. On the basis of a crystallographic structure[47] of the product of the low-temperature thermal hydrolysis of $[La(acac)_3(H_2O)_2]$ which shows formation of an $La_4(\mu_{4-}O)$ core and TEM data, it is reasonable that oxo-lanthanide(III) clusters are being formed in thermally treated polyimides with particle sizes of only several nanometers. The CTE lowerings are much greater than those observed with three-dimensional silica-polyimide hybrids and are on the order of those observed with exfoliated two-dimensional montmorillonite (silicate) sheets incorporated into PMDA/4,4′-ODA. Also, the increase in modulus for oxo-holmium(III)-6FDA/4,4′-ODA films parallels that reported for montmorillonite nanocomposites of PMDA/4,4′-ODA. Thus, in selected cases, the hydrolytic and thermal transformation of labile lanthanide(III) coordination compounds to oxo-metal(III) species leads to nanocomposite materials whose properties are enhanced in a manner similar to that induced by delaminated and randomly dispersed montmorillonite or other silicate sheet structures.

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