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Enhancement of Dimensional Stability in Soluble Fluorinated Polyimides via the in Situ Formation of Lanthanum(III)−Oxo−Polyimide Nanocomposites

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The synthesis and characterization of composite inorganic−polyimide films is described by adding diaquotris(2,4-pentanedionato)lanthanum(III) to soluble, low dielectric, colorless polyimides formed from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride/1,3-bis-(3-aminophenoxy)benzene (6FDA/APB), and 6FDA/2,2-bis[4-(4-aminophenoxy]hexafluoropropane (6FDA/BDAF). The $[La(acac)_3(2H_2O)_2]$-containing polyimide films were thermally treated from 220 to 340 °C which resulted in substantial lowering of the linear coefficients of thermal expansion at low metal concentrations (<4%) without sacrificing other essential thermal and mechanical properties of the parent polyimide. TEM data are consistent with particle sizes for the lanthanum ion-containing species which are in the nanometer range; thus, the visual clarity of the films was maintained. Refractive index measurements indicate that the films are isotropic. Addition of the lanthanum complex to the poly(amic acid) form of 6FDA/APB and 6FDA/BDAF followed by thermal curing to 300 °C yields low molecular weight crazed polyimide films.

Introduction

The management of the properties of organic macromolecules via the homogeneous incorporation of metal−oxo clusters on the nanometer scale within a polymer matrix is being actively pursued.[1−5] Such hybrid inorganic−organic nanocomposite polymeric materials can be synthesized via the exfoliation of sheet minerals such as organically modified montmorillonites and hectorites[6−9] and via sol−gel techniques using metal alkoxides[10−19] that yield metal−oxo phase particles of varying size and morphology depending upon hydrolytic conditions and the metal alkoxide structure. Hybrid materials can also be prepared via thermally and hydrolytically induced transformations of organometallic and metal complexes, such as dibenzenechromium, dodecacarbonyltriiron, and tris(β-diketonato)metal(III)

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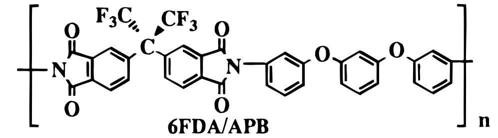
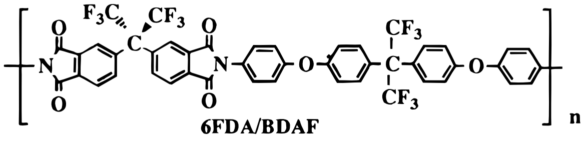
complexes of aluminum, iron, and lanthanides, which are in a polymer–solvent matrix prior to thermal curing.[20–22]

Relatively few studies of polyimide–inorganic composites with nanometer-sized inorganic oxide structures formed from the controlled hydrolysis/condensation of metal alkoxides and related compounds have been reported. This may be due in part to a predisposition that the properties of a polyimide formed from its poly(amic acid) can be compromised by the presence of water which is necessary to produce the metal–oxo phase. Thus, it would be desirable in preparing hybrid materials to utilize the fully imidized polymers which are much more hydrolytically stable. However, traditional cycloimidized polymers such as PMDA/ODA (derived from pyromellitic dianhydride and 4,4′-oxydianiline) are insoluble in common solvents, and thus, a homogeneous polyimide–inorganic oxo composite cannot be generated via a sol–gel approach.

There are a select number of polyimides that are soluble in organic media. In this paper we report attempts to develop an inorganic oxo phase in hexafluoroisopropylidene-containing polyimides that have soluble imidized structures. Such fluorinated polyimides have desirable properties for processing and electronic purposes; however, they often have linear coefficients of thermal expansion (CTE) that are well above those for metals and inorganic oxides or ceramics with which they might be bonded. The incorporation of inorganic materials at low weight and volume fractions in a polymer matrix has been shown to be effective in modulating the linear CTE. For example, recent research by Yano et al.[9f] and Pinnavaia et al.[6a,e] has demonstrated that the incorporation of low concentrations of silicate sheets (montmorillonite) into PMDA/ODA improves selected mechanical and thermal properties. On thermal curing of the silicate-doped poly(amic acids) visually clear films, demonstrating nanometer-sized particles, were obtained with lowered CTEs, markedly decreased gas permeability, and enhanced mechanical properties. For the related polyamides (Nylon 6) impregnated with exfoliated montmorillonite sheets, Kojima et al.[9h] reported enhanced strength, modulus, and heat distortion temperature. Sen et al.[17] and Tripathy et al.[23] have used primarily the water released in the thermal imidization of poly(amic acids) to prepare silica-like phases in polyimides for cluster-size-dependent catalytic and nonlinear optical purposes. Mark et al.,[11] Morikawa et al.,[24] Ober et al.,[25] and Ree et al.[26] have produced polyimide–silica hybrid materials via the hydrolysis of silicon tetraalkoxides. The effects of in situ silica loading on polyimide thermal, mechanical, and optical properties cannot be fully described by simple generalizations.

Specifically, this paper describes the synthesis and characterization of composite inorganic–polyimide films using diaquotris(2,4-pentanedionato)lanthanum(III) as the inorganic precursor and two soluble polyimides formed from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane (6FDA) and 1,3-bis(3-aminophenoxy)benzene (APB) or 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BDAF). A primary goal of this work was to control the linear CTE in these fluorinated polymer composites without adversely diminishing mechanical or other thermal properties. The polyimides, 6FDA/APB and 6FDA/BDAF, are representative of a growing class of fluorinated polyimides that for space and electronic applications have several desirable properties including: low dielectric constants, low moisture absorptivity, resistance to UV and electron radiation in nitrogen and in vacuo, enhanced processibility, and optical transparency in the visible while maintaining the thermal–oxidative stability associated with traditional polyimides.[27–34] Additionally, fluorinated polyimides are soluble as imides in a variety of solvents and have lower glass transition temperatures which leads to processing advantages.[35,36] However, 6FDA/APB and 6FDA/BDAF


6FDA/APB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have elevated CTEs (ca. 50 ppm/K) which limit their use in space applications including the fabrication of large inflatable solar reflectors and antennas where dimensional integrity is important in accurate focusing of radiant energy and in composite devices where CTE mismatches induce deleterious stresses.[37−39]

Our paper focuses on attempts to lower the linear CTE while maintaining the visual clarity of 6FDA/APB and 6FDA/BDAF films via the addition of the hydrolytically and thermally labile eight-coordinate (distorted square antiprismatic structure from X-ray) diaquotris(2,4-pentanedionato)La(III) complex,[40] [La(acac)$_3$(H$_2$O)$_2$], to dimethylacetamide (DMAc), *N*-methylpyrrolidinone (NMP), and 2-methoxyethyl ether (diglyme) solutions of imidized 6FDA/APB and 6FDA/BDAF. [La(acac)$_3$(H$_2$O)$_2$] was chosen as the inorganic precursor to a metal−oxo phase for several reasons. La(III) is a metal ion that has a single stable tervalent oxidation state with a very large crystal radius of 117 pm.[41] Coordination numbers for La(III) complexes are commonly eight and nine.[42] For example, primary hydration numbers for the Ln(III) ions in aqueous solution have been established at 8−9.[43,44] Thus, in La(III) we have a metal ion that has an expanded coordination sphere and is a hard Lewis acid, both allowing for enhanced binding to polymer donor atoms such as the imide functionality. Indeed, DMAc adducts of the Ln(III) ions are known such as Ln(ClO$_4$)$_3$·8DMAc (Ln = La and Nd) whose composition and properties suggest eight coordination.[45a] Polymer−metal coordination should be of pivotal importance in preventing the migration of metal(III) complexes to the surface of the film during thermal curing. Such metal−polymer coordination, or "site isolation" (Sen et al.[17,20]), leads to a uniform homogeneous distribution of nanometer-sized metal−oxo clusters throughout the polymer matrix which maintains visual clarity.[17,20,21,46,47] It was our expectation that the interaction of La−oxo clusters with polymer chains would lower the linear CTE. Beyond La(III) the Ln series is dominated by metal(III) species that are strongly paramagnetic and have distinctive fluorescence properties that can serve as probes of the ligand environment.[48,49]

Metal alkoxides have been the precursors of choice for the generation of inorganic−organic hybrid materials. While there has been impressive progress in the synthesis and characterization of Ln(III) alkoxides,[50] these alkoxides are reactive, and their synthesis and handling requires drybox or vacuum techniques. The use of mixed alkoxo-β-diketonato metal complexes has been reported to moderate the hydrolytic activity of alkoxides, such as those of titanium and zirconium, and give rise to smaller metal−oxo cluster sizes in polymers.[51−53] Metal−2,4-pentanedionate linkages are not as easily hydrolyzed as their alkoxide analogues; nonetheless, selected metal-2,4-pentanedionates are hydrolyzed at modest temperatures and can be thermally transformed to metal oxides.[54] This is especially true for [La(acac)$_3$(H$_2$O)$_2$] which, while air stable at 25 °C, becomes a glassy plastic solid when heated over the temperature range 80−95 °C.[55] This is not simply loss of coordinated water. TGA data show (discussed later) both the loss of 2,4-pentanedione and water.[56] Facile elimination of 2,4-pentanedione via hydrolysis with coordinated water has been observed directly via NMR in the Ln-like complex, [Y$_2$(OAc)$_2$(acac)$_2$(H$_2$O)$_2$], which gives free 2,4-pentanedione when dissolved in CDCl$_3$ at 25 °C.[57]

Finally, we chose to investigate [La(acac)$_3$(H$_2$O)$_2$] in soluble polyimides because recent X-ray data were disclosed that demonstrated that [La(acac)$_3$(H$_2$O)$_2$] is transformed, with the loss of 2,4-pentanedione and water, by mild heating to a tetranuclear 2,4-pentanedionate complex, [La$_4$(O)(acac)$_{10}$], with an tetrahedral La$_4$-(μ_4-O) core;[58] this is consistent with several recent reports of the "unexplained appearance of" and "incorporation of unexpected" μ-oxo [O^{2-}] groups[59] as polynuclear M$_x$(μ_x-O) cores formed particularly with oxophilic (lanthanides, actinides, and early transition elements) metal alkoxides. μ-Oxo ligands appear to be formed by hydrolysis and by thermally promoted cleavage of alkoxide C−O bonds,[60] and their presence can be rationalized as "a means of ensuring high coordination as encapsulated ligands in closo polyhedra".[59] Thus, with [La$_4$(O)(acac)$_{10}$] formed from [La(acac)$_3$(H$_2$O)$_2$] we have a ready route to an initial metal−oxo

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Table 1. Thermal and Mechanical Data for 6FDA/APB−Diaquotris(2,4-pentanedionato)lanthanum(III) Films as a Function of Cure Cycle (Solvent: DMAc)

cure cycle (°C)[a]	repeat to La(III) ratio[b]	CTE (ppm/K)	T_g (DSC, °C)	TGA 10% wt loss (°C)	tensile strength (Ksi)	percent extension at break	modulus (Ksi)	weight percent metal[c]
control 100, 200, 300	∞	48.5	208	515	17.6	5.0	448	0
100, 150, 200, 220	5.0	41.2	202	417	16.7	3.96	501	3.56 (3.82)
100, 150, 200, 250	4.8	32.6	207	444	15.2	3.12	538	3.65 (3.93)
100, 125, 150, 175, 200, 300	5.0	30.7	208	462	12.5	2.52	524	3.53 (3.80)
100, 150, 200, 340	4.8	34.0	207	447	15.4	3.41	505	3.63 (3.93)

[a] Details of the different cure cycles are contained in the Experimental Section. [b] Polymer repeat unit to La(III) ion mole ratio. [c] The first entry is calculated with $La(acac)_3$ remaining intact during thermal curing; the entry in parentheses is calculated based on polyimide and the initial lanthanum-2,4-pentanedionate complex reacting to give lanthanum(III) oxide.

phase. It was our expectation that $[La(acac)_3(H_2O)_2]$ would give nanometer-sized inorganic clusters in our polyimide matrixes and enhance polymer properties via a large interfacial area between the polymer and the inorganic phase.[3,9f,61]

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 (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 and La_2O_3 were obtained form Fisher and Aldrich, respectively. DMAc (HPLC grade) and diglyme (anhydrous 99.5%) were obtained from Aldrich; NMP was purchased from Spectrum.

Preparation of Diaquotris(2,4-pentanedionato)lanthanum(III). Commercially purchased complex was found to be quite impure and could not be improved with recrystallization. Thus, the lanthanum tris(acetylacetonate) complex was made following the general approach of Pope et al.,[55] Stites et al.,[40a] and Phillips et al.[40b] the latter preparing the complex on which an X-ray structure was done.[40b] Redistilled 2,4-pentanedione (50 mL) was combined with 15 M ammonia and water until the diketone went into solution as the ammonium salt. Lanthanum(III) chloride was prepared by dissolving lanthanum(III) oxide in 6 M hydrochloric acid. The pH was adjusted to 5.0 with sodium hydroxide. The ammonia solution of 2,4-pentanedione was added dropwise to the stirring $LaCl_3$ solution. The pH of this final solution was allowed to rise to 6 and held constant at this value to prevent precipitation of the rare-earth oxide. The solution was allowed to stir for 24 h, during which time a colorless crystalline product formed. The product was filtered, washed twice with deionized water, and dried in air for 4 h, after which it was recrystallized from 95% ethanol. The final crystals were dried under vacuum for several hours. Composition of two samples to La_2O_3 at 850 °C gave a water to $La(acac)_3$ ratio of 2.02:1.00.

Preparation of the Polyimides. Imidized 6FDA/APB powder was obtained by the addition of 6FDA (0.5% molar excess) to a DMAc solution of 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 three 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/BDAF powder was prepared similarly with a 1% 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, 00 g/mol.

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% solids solution. The solutions were stirred 2−4 h to dissolve all of the polyimide. The clear metal-doped resins were cast as films onto glass plates using a doctor blade set to give cured films near 25 μm. The films were allowed to sit for 15 h at room temperature in flowing air at 10% humidity and then were cured in a forced air oven and removed from the plate by soaking in deionized water.

Imidized 6FDA/APB powder was obtained by the addition of 6FDA (0.5% molar excess) to a DMAc solution of APB to first prepare the poly(amic acid) at 15% solids (w/w). The reaction was stirred at the ambient temperature for 7 h. The inherent viscosity of the polyamic acid was 1.4 dL/g at 35 °C. This amic acid precursor was chemically imidized in an acetic acid−pyridine solution, precipitated with methanol, washed thoroughly with deionized water, and vacuum-dried at 200 °C for 20 h. The inherent viscosity in DMAc was 0.81 dL/g at 35 °C. GPC gave M_n at 85 000 g/mol and M_w at 288 000 g/mol. Imidized 6FDA/4-BDAF powder was prepared similarly with a 1% 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.

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% solids (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 near 1 mil. The films were allowed to sit for 15 h at room temperature in flowing air at 10% humidity. This resulted in a film that 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 °C 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 °C 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 °C for 1 h. The films were removed from the plate by soaking in deionized water.

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Table 2. Thermal and Mechanical Data for 6FDA/BDAF−Diaquotris(2,4-pentanedionato)lanthanum(III) Films as a Function of Cure Cycle (Solvent: DMAc)

cure cycle (°C)[a]	repeat to La(III) ratio[b]	weight percent metal[c]	CTE (ppm/K)	T_g (DSC, °C)	TGA 10% wt loss (°C)	tensile strength (Ksi)	percent extension at break	modulus (Ksi)
control 100, 200, 300	∞	0	51.2	266	515	13.5	6.1	337
100, 150, 200, 220	5.0	2.73 (2.89)	40.3	280	466	15.3	7.1	371
100, 150, 200, 250	5.1	2.69 (2.84)	40.1	274	481	14.6	6.3	349
100, 150, 200, 250	3.9	3.45 (3.70)	32.6			not measured		
100, 125, 150, 175, 200, 300	4.9	2.78 (2.94)	38.7	268	477	15.8	7.5	343
100, 150, 200, 300	3.9	3.45 (3.70)	29.4			not measured		
100, 150, 200, 340	4.8	2.80 (2.96)	41.5	267	490	15.1	7.9	330

[a] Details of the different cure cycles are contained in the experimental section. [b] Polymer repeat unit to La(III) ion mole ratio. [c] The first entry is calculated with La(acac)$_3$ remaining intact during thermal curing; the entry in parentheses is calculated based on polyimide and the initial lanthanum-2,4-pentanedionate complex reacting to give lanthanum(III) oxide.

Table 3. Thermal, Mechanical, and Optical Data for 6FDA/APB−Diaquotris(2,4-pentanedionato)lanthanum(III) Films as a Function of Solvent[a]

solvent	repeat to La(III) ratio[b]	CTE (ppm/K)	T_g (DSC, °C)	TGA 10% wt loss (°C)	tensile strength (Ksi)	percent extension at break	modulus (Ksi)	weight percent metal[c]	refractive index	
									n_{TE}[e]	n_{TM}[e]
DMAc (control)	∞	48.5	208	515	17.6	5.0	448	0	1.6084	1.6052
diglyme (control)	∞	50.4	208	506	16.4	4.7	433	0	*f*	*f*
NMP (control)	∞	46.3	209	494	17.8	4.5	478	0	*f*	*f*
DMAc	4.8	31.1 (32.9)[g]	208	430	16.4	3.4	550	3.63 (3.94)	1.6137	1.6118
diglyme	4.8	32.5	208	447	14.7	3.1	512	3.63 (3.91)	1.6116	1.6096
NMP	4.5	32.8	213	432	*d*	*d*	*d*	3.85 (4.17)	1.6157	1.6145

[a] For all films the cure cycle was 100, 200, 300 °C, 1 h at each temperature. [b] Mole ratio of polymer repeat units to La(III) ions. [c] The first entry is calculated with La(acac)$_3$ remaining intact during thermal curing; the entry in parentheses is calculated based on polyimide and the initial lanthanum-2,4-pentanedionate complex reacting to give lanthanum(III) oxide. [d] The film was too brittle and fragile to obtain satisfactory samples for mechanical measurements. [e] TE and TM represent transverse electric and transverse magnetic fields, respectively. [f] Not measured. [g] Film at the same concentration but with excess water added at a 15:1 mole ratio water:La(acac)$_3$(H$_2$O)$_2$.

Table 4. X-ray Photoelectron Spectroscopy Surface Composition for [La(acac)$_3$(H$_2$O)$_2$]−6FDA/APB Composite Films of Table 3 at the Air Side (All Films Cured to 300 °C, Relative Atomic Percent)

solvent for 6FDA/APB film[a]	repeat to La(III) ratio[a]	weight percent metal[b]	La	F	C	O	N
control (calc)	∞	0	0	11.8	72.5	11.8	3.9
control (found)	8	0	0	12.7	69.4	14.0	3.9
DMAc	4.8	3.63	0.57	2.8	74.4	17.8	4.5
diglyme	4.8	3.63	0.21	5.1	69.6	18.6	6.9

[a] The thermal cure cycle was 100 for 1 h, 150 for 1 h, 200 for 1 h and 300 for 1 h.

Thermogravimetric analysis, differential scanning calorimetry, and thermal expansions measurements were performed with Seiko TG/DTA 220, DSC 210, and TMA 100 systems, respectively. CTE measurements were done over the range of 70−125 °C. Micrographs were obtained with a Zeiss CEM 902 TEM. X-ray data were obtained with a Philips 3600 diffractometer. Refractive indices were obtained with a Metricon Model 2010 prism coupler. Mechanical measurements were made at ambient temperature on a Sintech Model 2000/2 tabletop load frame. Refractive index measurements were done on a Model 2010 prism coupler.

Results and Discussion

Synthetic Considerations. Tables 1−4 present the films that were synthesized and characterized in this study. Our expectation was that the inorganic phase formed via hydrolysis and thermal curing would result in a tailored lowering of the linear CTE without compromising polymer properties and would preserve film clarity. The preservation of film clarity requires the formation of a nanometer-sized inorganic phase in the cured polymer. To achieve nanoparticles, it is imperative that the La(III) additive be soluble in solutions of the polyimide and in the solvent free polyimide matrix that develops as solvent is lost in the thermal treatment. [La(acac)$_3$(H$_2$O)$_2$] is a soluble complex and is readily prepared by literature procedures as an eight-coordinate mononuclear white crystalline solid.[40,55] (Analytical data for two samples prepared in this work gave 2.02 (±0.03) mol of water/La(acac)$_3$ unit.) [La(acac)$_3$(H$_2$O)$_2$] is soluble in DMAc, NMP, and diglyme, and it remains dispersed in the uncured tact-free (ca. 35% solvent) polymer films. During thermal treatment of the doped films no phase separation of an inorganic component is visually apparent. Films were typically prepared at a molar concentration of polymer repeat unit-to-metal of ca. 5:1; concentrations of the complex greater than ca. 3:1 gave films which fractured on handling. We chose to prepare films from three solvents: DMAc, NMP, and diglyme. DMAc and NMP are polar aprotic solvents of high dielectric constant (38 and 32, respectively) and are excellent solvents for polyimides. NMP boils (202 °C) much higher than DMAc (165 °C), and we thought that it might enhance migration and aggregation of inorganic clusters by plactizing the polymer over a wider temperature range than DMAc. Amide solvents form strong interactions with polyimides and their precursors.[62,63] Diglyme, as a polyether, is much less polar than amides with a dielectric constant of ca. 5.7, and the ether linkages are in general less reactive than amide groups. All three solvents readily dissolve imidized 6FDA/APB and 6FDA/BDAF.

We chose [La(acac)$_3$(H$_2$O)$_2$] as the metal−oxo precursor because TGA data (Figure 1) make it clear that this complex undergoes significant thermal/hydrolytic deg-

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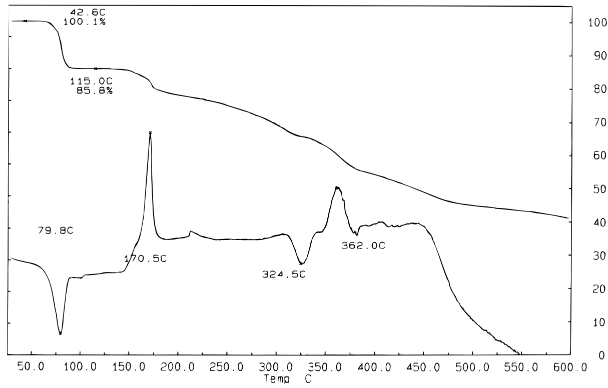

Figure 1. Thermal gravimetric curve for [La(acac)$_3$(H$_2$O)$_2$] run in air. (The initially lower trace is the DTA curve.)

radation at surprisingly low temperatures. From ca. 75 to 85 °C there is rapid weight loss to give a derivative which is stable from ca. 90 to 150 °C. The observed weight loss in this temperature regime is 14.3%, which is close to the formation of the tetranuclear complex [La$_4$O(C$_5$H$_7$O$_2$)$_{10}$] with one molecule of water/La. Above 150 °C there is continual degradation toward La(III) oxide (verified by X-ray powder diffraction). We felt that this early and facile thermal transformation of [La(acac)$_3$(H$_2$O)$_2$] to an initial polynuclear nanometer-sized metal−μ-oxo species could be important in modifying polymer film properties for the following reason. We have previously examined 6FDA/APB films doped with ineffective lanthanide(III) acetate tetrahydrates and tris(1,3-diphenyl-1,3-propanedionato)lanthanide(III) complexes.[64] With films cured at temperatures up to 300 °C under conditions similar to those described in this paper, five tris(1,3-diphenyl-1,3-propanedionato) complexes (Ce, Eu, Gd, Er, and Tm) studied gave an average CTE lowering of only 1 ppm/K and six tris(acetato) tetrahydrates (Dy, Ho, Er, Tm, Yb, and Y) gave an average lowering of only 3 ppm/K. When one looks at the TGA curves (Figure 2) for a typical Ln(III) acetate (yttrium) and tris(1,3-diphenyl-1,3-propanedionato)Ln(III) (neodymium) complex, one sees that the these complexes are quite thermally stable relative to [La(acac)$_3$(H$_2$O)$_2$]. Ten percent weight loss for the Y(III) acetate occurs at ca. 320 °C; for the tris(1,3-diphenyl-1,3-propanedionato)Nd(III) complex it is ca. 340 °C. Thus, to achieve a lowered CTE it seems essential for the Ln additive to be hydrolytically and/or thermally labile in being transformed toward a metal−oxo phase under the cure conditions. We anticipated that the more easily hydrolyzed/thermalized diaquotris(2,4-pentanedionato) complex of La(III) might give the desired CTE lowerings. Indeed, this was observed as seen in Tables 1−4 where CTE measurements were made over the range 70−125 °C.

Film Properties. Table 1 contains thermal and mechanical data for 6FDA/APB films cast from DMAc as a function of the cure cycle. It is common to subject polyimides to a final cure temperature near 300 °C to

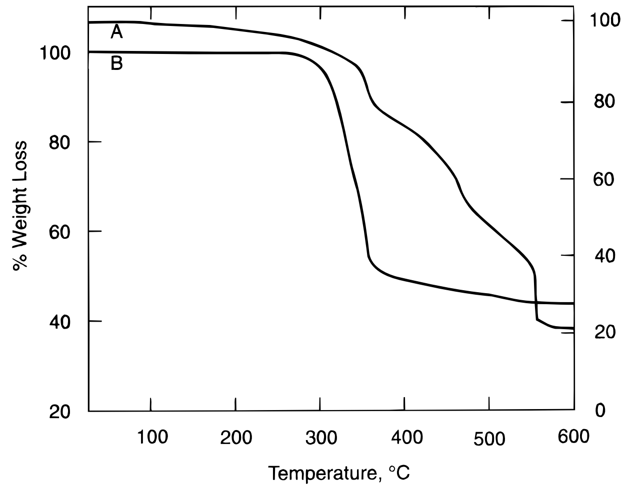

Figure 2. Thermal gravimetric curve for ytterium(III) acetate (A) and tris(1,3-diphenyl-1,3-propanedionato)neodymium(III) (B) run in air. (Right ordinate is for the Nd complex; left ordinate is for the Y complex.)

ensure imidization and remove solvents such as DMAc which bind tightly with polyimide structural units. Aromatic compounds are known to interact strongly with DMAc.[62,63] Since 6FDA/APB is a soluble polyimide, it can be applied and used as a coating at temperatures below those needed to imidize poly(amic acid) precursors. Thus, it was of interest to see if the CTE would be diminished at cure temperatures lower than the standard 300 °C. From the data in Table 1 there are marked lowerings of the CTE (15%) when the sample is cured to a maximum of 220 °C. The CTE decreases as the final cure temperature rises from 220 to 300 °C. At 340 °C the CTE increases slightly from its value at 300 °C. Thus, to achieve the maximum CTE lowering a temperature of ca. 250 °C is required after which going to final cure temperatures of 340 °C has little additional effect. The maximum CTE lowering is 37% which is striking considering the very low weight percent (<4%) of metal in the polymer. It is interesting to compare our results with the synthesis of silica−PMDA/ODA hybrid films reported by Morikawa et al.[65] The parent polyimide of their study had a linear CTE of ca. 47 ppm/K. At 30% silica the CTE decreased only to ca. 45 ppm/K, and at 70% silica the CTE was ca. 26 ppm/K. Thus, there is a strikingly larger CTE reduction on a per unit metal oxide basis with La relative to Si. What the origin of this large CTE reduction at such low loads is unknown to us at present. The particle size in the Morikawa et al. study at higher loadings was on the micron scale as determined by microscopy. Thus, our much smaller particle size (>5 nm; see Figure 4) may be a crucial factor. In this vein it is interesting to note that with the montmorillonite silicate sheets in PMDA-4,4′-ODA studied by the Toyota group (Yano et al.[9f]), where there is intimate polyimide−inorganic contact due to the exfoliation of the clay sheets, there is a large CTE reduction at low silicate loads. For example, the CTE in the PMDA/ODA clay hybrid at 150 °C in the parent polymer was 57 ppm/K, whereas at a 4 wt % silicate load the CTE dropped to 41 ppm/K.

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Table 2 presents thermal and mechanical data for 6FDA/BDAF−[$La(acac)_3(H_2O)_2$] films prepared in DMAc. As was observed with the 6FDA/APB films of Table 1, there is a decrease (ca. 20%) in the linear CTE. In contrast to the 6FDA/APB-doped films, the lowering of the CTE in the 6FDA/BDAF-[$La(acac)_3(H_2O)_2$] series at ca. 2.7% metal is essentially independent of the maximum cure temperature, which ranges from 220 to 340 °C. While the CTE reduction is generally less for the BDAF films relative to their APB congeners, this is attributable to the fact that while the polymer repeat unit-to-metal ratios are similar, the weight percent of the metal in the BDAF films is ca. 25% lower than in the APB films. When 6FDA/APB and 6FDA/BDAF films with similar weight percents of La are compared the CTE lowerings are much closer for the two composite materials. Thus, it appears that the lowering of the CTE is related more to the weight percent of additive than to the mole ratio of repeat unit-to-metal. Again, with 6FDA/BDAF films curing to 340 °C causes the CTE to increase slightly after having reached a minimum near 300 °C. It is interesting to note that in the 6FDA/BDAF series of Table 2, the CTE lowering is essentially independent of curing the films to final temperatures which are both above and below T_g. Thus, the mechanism of CTE lowering does not strongly involve enhanced chain mobility that comes above T_g which might allow increased particle aggregation and more optimal inorganic phase−polymer interactions. In contrast to the APB composite films where T_g was essentially unchanged relative to the control film, the BDAF analogues show a 14 and 8 K increase in T_g at final cure temperatures of 220 and 250 °C, respectively; at final temperatures of 300 and 340 °C T_g returns to that of the parent polymer. This modest increase in T_g at lower temperatures could reflect weak cross-linking of the polymer chains by the inorganic oxo phase. Covalent cross-linking is well-known to increase T_g markedly.[66] It has also been observed that coordination of chain segments to metal ions can increase T_g. In particular, Shim et al.[67a] examined polycarbonate films doped with ruthenium(III) chloride trihydrate and found that T_g for a 10 wt % Ru(III) film increased from 150 °C for the pure polymer to 233 °C. Infrared data showed that Ru(III) was coordinated to carbonate C=O groups. With tris(triphenyphosphine)chlororhodium(I)[67b] and Pd(II) acetate[67c] incorporated into cellulose acetate, the T_g elevations for 10 wt % composites were 7 and 10 °C, respectively. With our similar La(III) species we might have expected to see an elevated T_g if there were strong coordinative interactions of polymer with metal. Since T_g is very nearly the same as the parent polymer in all of our DMAc and diglyme samples at a final temperature of 300 °C, any coordinative cross-linking interactions must be weak. Such a weak interaction would be consistent with the fact that the amide and phenyl ether donors are only weakly Lewis basic or with the presence of La−oxo clusters in which the metal ions are substantially coordinated by O^{2-} ligands. David and Scherer[68b] 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 found that the in situ precipitation of SiO_2 at 20−30 wt % in poly(diemthylsiloxane) "does not affect the T_g".[22] Thus, with the low weight percents of La(III) used in our work and the minimal changes in T_g with silicon−oxo phases, it is not unexpected that the La-doped films of this work show minimal changes in polymer T_g. The large effective surface area of the inorganic phase clusters in this study may be responsible for the substantial CTE reductions.

All the films of Tables 1 and 2 remain have mechanical properties that are close to those of the parent polymer. In most cases the tensile modulus increases slightly, yet the films remain flexible.

Solvent effects on film synthesis were obtained by casting [$La(acac)_3(H_2O)_2$]−6FDA/APB solutions from DMAc, NMP, and diglyme. Table 3 displays characterization data for these films. All films were visually transparent, uniform in thickness, and free from bubbles and distortions. The properties of the metal-free parent polyimide films cured to 300 °C are essentially independent of solvent. However, the properties of La−cetylacetonate-doped films are significantly solvent dependent. All films show a pronounced diminution of the CTE at a low level of La(III) compared with traditional "filler" composites using micron-sized particles. The metal-containing films prepared from diglyme are flexible and can be tightly creased without fracture similar to the control film. The DMAc films are also substantially flexible and can be softly creased. The NMP film was very different in appearance and properties relative to the diglyme and DMAc films. This latter film was clear, but very dark, and came off the glass casting plate with a crazed and fractured structure. The glass transition temperature was elevated relative to the other films, and the film fragments were very brittle such that samples for mechanical measurements could not be cut. Thus, NMP is not a satisfactory solvent. From refractive index measurements of η_{TE} and η_{TM}, the films appear to be isotropic as would be expected for the flexible parent polyimides. The films cast from diglyme are much less colored then those cast from DMAc; in all cases the films are visually transparent.

X-ray diffraction data (Figure 3) for all La-containing films show only the broad peaks which are the amorphous halos attributable to the polyimides. From the sol−gel hydrolysis of metal alkoxides[69] it is common to have a metal−oxo phase formed which is amorphous. However, it may also be that X-ray reflections are not observed due to Scherrer broadening[70] due to very small particle size. Representative TEMs are shown in Figure 4 for a 5:1 6FDA/BDAF film prepared from diglyme and a 5:1 6FDA/APB film in DMAc. In neither film can discrete particles be seen consistent La(III) particle sizes

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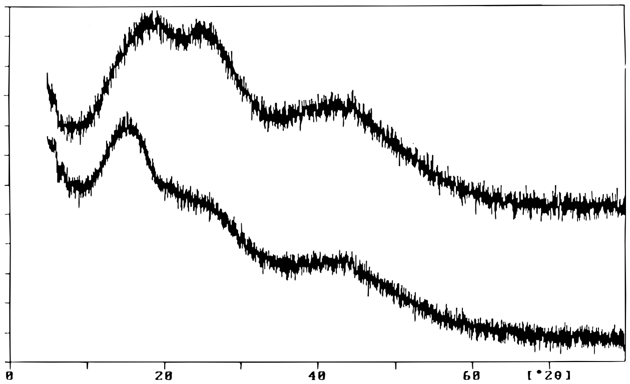

Figure 3. X-ray diffraction data for $[La(acac)_3(H_2O)_2]$-doped 6FDA/APB in diglyme at 4.8:1 and cured to 300 °C (A) and for $[La(acac)_3(H_2O)_2]$-doped 6FDA/BDAF in DMAc at 4.9:1 and cured to 300 °C. (The ordinate is arbitrary counts.)

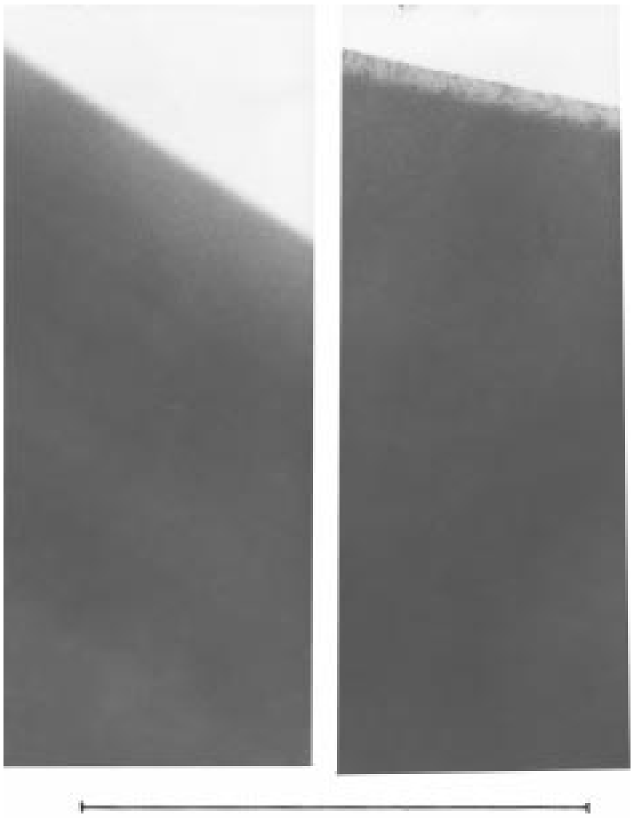

Figure 4. Transmission electron micrographs for $[La(acac)_3(H_2O)_2]$-doped 6FDA/APB in DMAc at 4.8:1 and cured to 300 °C (A) and for $[La(acac)_3(H_2O)_2]$-doped 6FDA/BDAF in diglyme at 5.2:1 and cured to 300 °C. (The scale bars are 1 μm.)

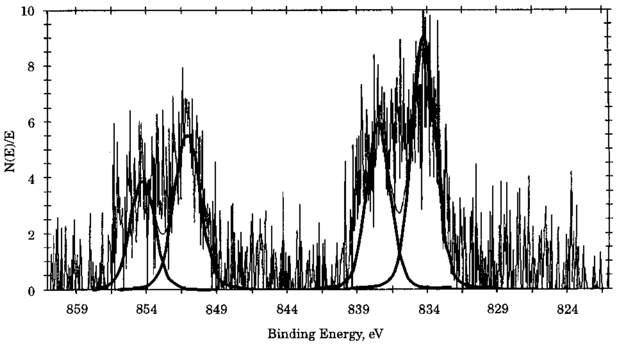

Figure 5. X-ray photoelectron spectrum and curve fit in the La 3d region for $[La(acac)_3(H_2O)_2]$-doped 6FDA/APB in DMAc at 4.8:1 and cured to 300 °C.

Table 5. Concentration Dependence of CTE for 6FDA/APB−Diaquotris(2,4-pentanedionato)lanthanum(III) Films Cast from a Mixed Solvent of Diglyme/DMAc[a]

polymer repeat unit to metal(III) mole ratio[b]	control (0)	16.1:1 (1.2)	9.9:1 (2.0)	6.8:1 (2.8)	4.8:1 (3.9)
linear CTE (ppm/K)	48.5	45.0[c] 44.9 45.0	43.2	40.3	31.1

[a] Diglyme is 55% by weight. [b] The values in parentheses are the weight percent metal based on the La_2O_3 remaining in the polyimide after thermal curing to 300 °C. [c] Values for three separate determinations.

being on the order of a few nanometers. TEMs also suggest that there is an essentially homogeneous distribution of La(III) particles throughout the polymer matrix. The presence of nanometer-sized particles is consistent with the interaction of polymer with a La(III) mononuclear or cluster species, which prevents separation of an inorganic phase with migration to the film surface. If there is no interaction of the inorganic species with the polymer, we expect migration to the surface. We have amply demonstrated such migratory behavior with these two fluorinated polymer and other polyimides in which we have thermally promoted reduction of a polymer soluble Ag(I) complex to metallic Ag; the metallic atoms/clusters of Ag(0), which clearly do not possess the capability to bond to the polymer, migrate significantly to give reflecting and conducting surfaces.[71] This supports the concept of "site isolation" suggested by Sen and co-workers[20] as being important to forming nanophases in polymer matrixes. Table 4 shows XPS composition data for three of the 6FDA/ODA films of Table 3. These surface data show clearly that there is minimal migration of La species to the surface. For films cured in diglyme and DMAc the La atom percents at the surface are 0.21 and 0.57, respectively. It is interesting to note that La-containing films have enhanced oxygen at the surface relative to the control. We suspect that this is due to some metal-promoted or -catalyzed oxidation at the polymer surface. Finally, Figure 5 displays the La 3d XPS region which shows two distinct La peaks separated by ca. 3 eV for 6FDA/APB in DMAc at a repeat unit-to-metal ratio of 4.8:1. A virtually identical pattern is seen for this same polyimide in diglyme at the 4.8:1 ratio. (The $3d_{3/2}$ and $3d_{5/2}$ peaks are separated by 16.8 eV.) This clearly suggests two different La environments and is not inconsistent with very small inorganic phase particle sizes which could lead both to interior and surface different La species in similar concentrations.

The data in Table 5 present the lowering of the CTE for 6FDA/APB as a function of La concentration from a

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(70) Scherrer, P. *Gottinger 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.

(71) (a) Caplan, M. L.; Southward, R. E.; Thompson, D. W.; St. Clair, A. K. *Proc. Am. Chem. Soc., Div. Polym. Mater.: Sci. Eng.* **1994**, *71*, 787. (b) Southward, R. E.; Thompson, D. S.; Thompson, D. W.; Caplan, M. L.; St. Clair, A. K. *Proc. Am. Chem. Soc., Div. Polym. Mater.: Sci. Eng.* **1995**, *73*, 382−383. (c) *Ibid. Chem. Mater.* **1995**, *7*, 2171−2180. (d) *Ibid.* Preparation of Silvered Polyimide Mirrors Via Self-Metallizing Poly(amic acid) Resins; *Metal-Containing Polymeric Materials*; Pittman, U. C.; Carraher, C. E., Culbertson, B. M., Zeldin, M., Sheets, J. E., Eds.; Plenum: New York, 1996; pp 349−356.

repeat-to-metal ratio of 16:1 to 5:1. The CTE decreases slowly but significantly as the weight percent of metal increases to 2.8. But between 2.8 and 3.9% the lowering is striking. Increasing the concentration of La >4% begins to give films that are clear but more prone to fracture with creasing.

A natural question to consider is whether $[La(acac)_3(H_2O)_2]$ could be placed into the poly(amic acid) precursor to give the metal–oxo–polyimide hybrid. We examined this option by placing $[La(acac)_3(H_2O)_2]$ into the poly(amic acid) of 6FDA/APB. However, thermal treatment of the doped amic acid films gives only crazed and brittle films, which is consistent with the La(III) additive leading to compromised chain molecular weight. Young et al.[72] have shown that in the curing of the poly(amic acid) of 6FDA/BDAF to the polyimide there is a large decrease in molecular weight ($M_w = 197\,000$ D to $M_w = 39\,000$ D) as the cure temperature increases; the greatest diminution occurs in the 125–200 °C range. Further heating to 300 °C again increases the molecular weight ($M_w = 106\,000$ D). The presence of the metal(III) species may coordinate to shortened chain ends and keep the molecular weight from building up again as imidization continues. Thus, it is essential to use the imidized form of these polyimides with metal–2,4-pentanedionate dopants.

Another question to ask is this: will any metal–acetylacetonate complex that is soluble in the subject polyimides thermalize to an oxide phase leading to a CTE lowering. To pursue this question we looked at 6FDA/APB and 6FDA/BDAF containing tris(acetylacetonato)aluminum(III) at the 5:1 ratio. Curing these films to 300 °C gave only a modest reduction in CTE values in DMAc and diglyme, 45.4 and 44.1 ppm/K, respectively. Tetrakis(acetylacetonato)zirconium in 6FDA/APB in DMAc gave a film with a 6% lower CTE. Both Al(III) and Zr(IV) have much smaller radii than La(III). Bergmeister and Taylor[22] found that tris(2,4-pentanedionato)iron(III) when added to the poly(amic acids) of BTDA/ODA and PMDA/ODA and thermally cured gave dark brown to black films "some [of which] were flexible; however, all the films fractured when creased". Thus, there does appear to be singular chemistry involved with $[La(acac)_3(H_2O)_2]$ that is not general to all acetylacetonate complexes.

Finally, we asked ourselves if the property modifications seen in our fluorinated soluble polyimides were due to the $[La(acac)_3(H_2O)_2]$ complex or simply due to a liberated La(III) ion produced on thermal/hydrolytic degradation of the complex. We examined several simple soluble salts of several lanthanides such as nitrates and chlorides that generate a simple solvated Ln(III) ion in the polyimide–DMAc solution. When films are prepared with these additives, they are brittle, discolored, and bubbled. Furthermore, we have examined several hexafluoroacetylacetonate, trifluoroacetylacetonate, and trifluoroacetate complexes. These complexes give severely bubbled, brittle, and discolored films. Thus, we believe that the chemistry involved with the La–acetylacetonate complex in forming an inorganic–polyimide hybrid material is singular. We are pursuing mixed lanthanide alkoxide–β-diketonate systems in an attempt to gain control of the metal–oxo phase in terms of particle size and morphology.

Conclusions

The addition of the eight coordinate diaquotris(2,4-pentanedionato)lanthanum(III) complex at very low weight percents to DMAc and diglyme solutions of the soluble polyimides 6FDA/APB and 6FDA/BDAF gives CTE lowerings up to a maximum of ca. 40% while maintaining essential mechanical and thermal properties and the visual clarity of the parent polymers. On the basis of a crystallographic structure of the product of the thermal hydrolysis of $[La(acac)_3(H_2O)_2]$ which shows formation of an $La_4(\mu_4\text{-}O)$ core, the TGA curve for $[La(acac)_3(H_2O)_2]$, and TEM data, it is reasonable that a La–oxo cluster is being formed with particle sizes on the nanometer level. The CTE lowerings are much greater than those observed with silica–polyimide hybrids and on the order of those of exfoliated montmorillonite (silicate) sheets incorporated into PMDA/ODA.

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