

Molecular Level Ceramic/Polymer Composites. 2.¹ Synthesis of Polymer-Trapped Silica and Titania Nanoclusters

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The concept of "site isolation" was used to synthesize SiO₂ and TiO₂ nanoclusters trapped in polyimide matrices. M(OEt)₄ (M = Si, Ti) was added to polyamic solutions derived from 4,4'-oxydianiline and either 1,2,4,5-benzenetetracarboxylic acid dianhydride or 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride. Following thermal curing, polyimide films containing a homogeneous dispersion of SiO₂ or TiO₂ particles were obtained. Oxide nanoclusters (size <1-1.5 nm) were present in polyimide films containing 12% TiO₂ and up to 32% SiO₂. However, 1- μ m particles were present at 42% SiO₂ content. Two-micrometer particles were formed even in 12% SiO₂ containing films when poly(diethoxysiloxane), rather than Si(OEt)₄, was used as the oxide precursor.

The demand for materials with novel combinations of properties has led to the recent efforts in modification of known polymers via the incorporation of a variety of additives. Ceramic nanoclusters with sizes ranging from <1 to 10 nm represent a new class of materials with properties that are different from those of discrete molecules, as well as bulk solid-state materials.³ Their anticipated applications range from cluster-size-dependent catalysis⁴ to nonlinear optics.⁵ In many of these applications, the ability to form films and fibers is an important requirement. This is most easily achieved by forming composites in which nanoclusters are embedded in a processable polymer matrix. A further advantage of synthesizing such a composite is that the polymer matrix will physically prevent the agglomeration of the clusters—a persistent problem in size-selective cluster synthesis.

Aromatic polyimides have long been the material of choice in industry because of their high thermal stability, chemical resistivity, and mechanical strength.⁶ It was, therefore, of interest to see if ceramic nanoclusters could be formed in a polyimide matrix. The high glass transition temperatures (T_g) of polyimides would be expected to further stabilize the nanoclusters by decreasing their mobility, thereby preventing their agglomeration to larger clusters. In the present study, we have chosen to make silicon and titanium dioxide clusters because of their ex-

Table I. Analysis of MO₂ in Polyimides

polyim	% calcd	% found
BTDA-ODA/TiO ₂	14.0	11.9
PMDA-ODA/SiO ₂	14.0	6.0
	44.0	13.7
	44.0	42.2 with H ₂ O ^a
	34.0	32.0 with H ₂ O ^a

^a 1.3 mol of H₂O/mol of Si(OEt)₄, together with a trace of HCl, was added prior to curing.

pected interesting catalytic and electronic applications.⁷

The formation of metal oxide containing polyimides by the incorporation of metal compounds into the precursor polyamic acid prior to curing has been reported.^{1,8} However, a nonhomogeneous distribution of the oxide particles with markedly higher concentration at or near the polymer surface was often observed.⁸ In addition, large particles with sizes >100 nm are usually formed.⁸ In our approach to the synthesis of polymer-trapped nanoclusters, we have used the concept of "site isolation". The basic idea is to synthesize and maintain the clusters in isolated pockets in the polymeric matrix, and we achieve this by (a) pre-binding the oxide precursor to specific sites on the polymer backbone and (b) chemically relating the formation of the ceramic material from the precursor with the final curing

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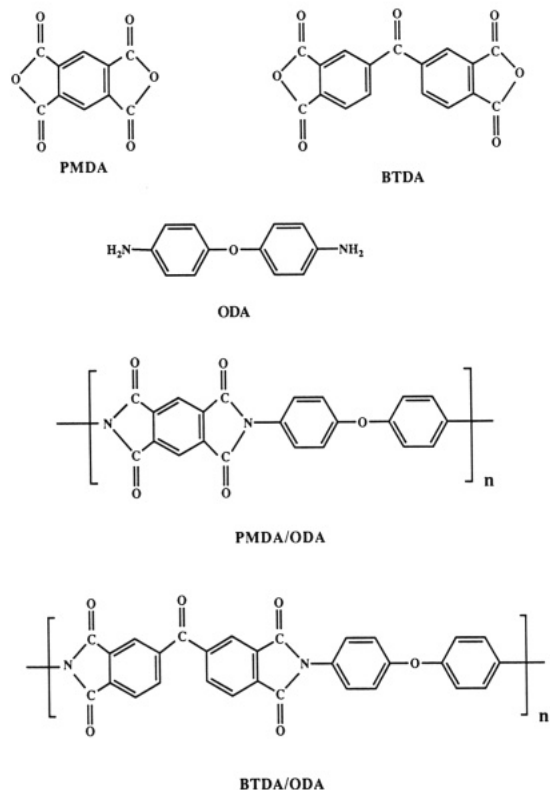
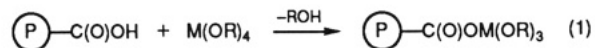


Figure 1. Chemical structures of monomers and polymers.

of the polymer. As described below, we have synthesized molecular level ceramic/polymer composites containing high concentrations of silica and titania nanoclusters distributed homogeneously in polyimide matrices.

Results

The polymers chosen for our studies have structures depicted in Figure 1 (ODA = 4,4'-oxydianiline; PMDA = 1,2,4,5-benzenetetracarboxylic acid dianhydride; BTDA = 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride). The sequence of steps involved in generating the oxide nanoclusters in polyimide matrices is outlined in Figure 2. The polyamic acid precursor formed initially possesses carboxylic acid groups, which are expected to act as binding sites for the metal alkoxides⁹ (eq 1). During the



imidization step leading to ring closure, water is released and results in the hydrolysis of the alkoxides to eventually generate the oxides. The rigidity of the polyimide backbone (as evidenced by their high T_g) slows down the mobility of the oxide clusters formed and prevents agglomeration to large particles. The possible coordination of the polyimide carbonyl groups would also be expected to impede cluster mobility.

Upon curing to the fully imidized polymer, both PMDA-ODA and BTDA-ODA formed free-standing transparent golden-yellow films. In the case of the doped polymers, the initial homogeneous solution containing the alkoxide and the polyamic acid was golden-yellow and also gave transparent, flexible, free-standing golden-yellow films upon curing (Figure 3). The only exceptions were the films incorporating 42% SiO₂, which yielded translucent, rather than transparent, films of lowered flexibility.

Analysis of the dopant level in the polyimide films (Table I) showed that the titania content was close to the calculated value. But in the case of the silica-doped po-

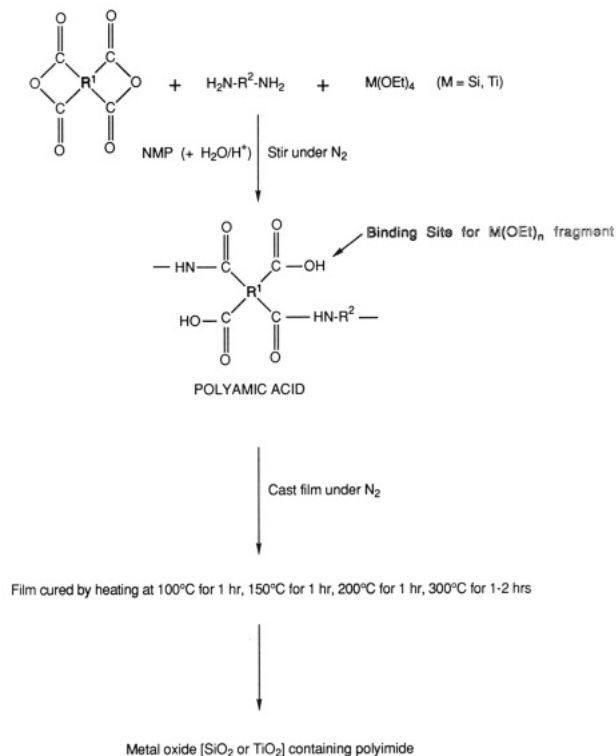


Figure 2. Steps involved in the synthesis of polymer-trapped oxide nanoclusters.

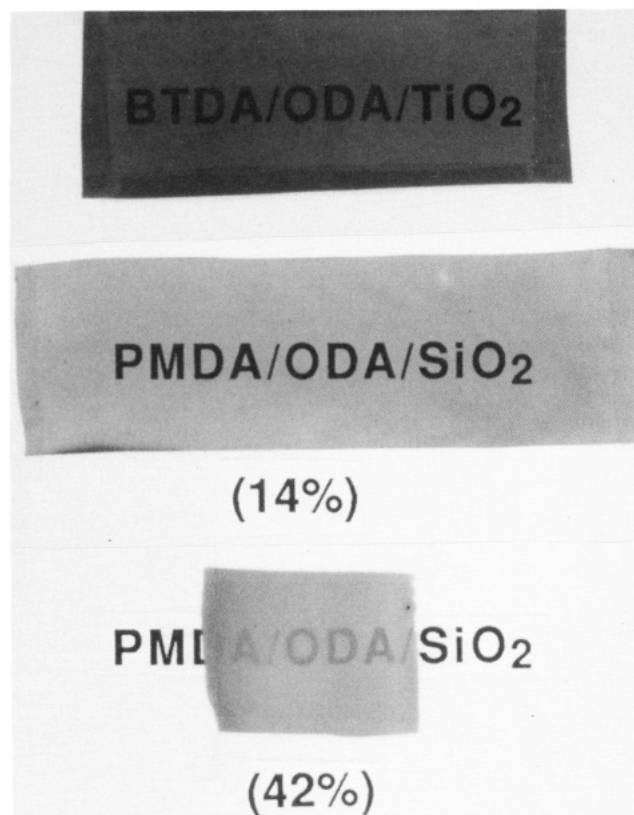


Figure 3. Photographs of free-standing polymer films of BTDA-ODA/TiO₂ (12%), PMDA-ODA/SiO₂ (14%), and PMDA-ODA/SiO₂ (42%).

lyimides, a considerable amount of the dopant was lost. This dopant loss suggested incomplete hydrolysis and volatilization of the precursor, Si(OEt)₄, during the thermal imidization process. The difference between titanium and silicon is, of course, a consequence of the significantly slower hydrolysis rates for the alkoxides of the latter ele-

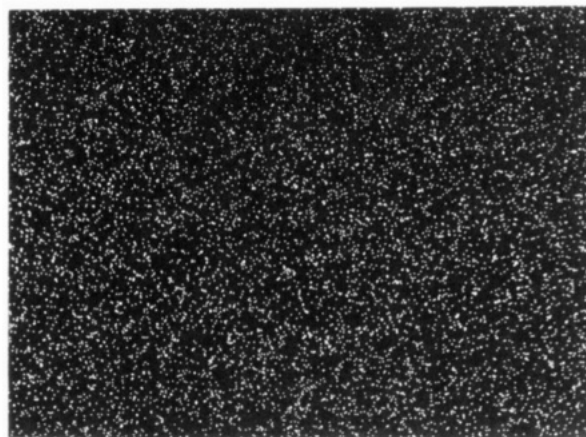
TOP PMDA ODA SiO₂ (6%) : Si X-RAY MAPTOP PMDA ODA/SiO₂ (42%) : Si X-RAY MAP

Figure 4. X-ray dot maps of PMDA-ODA/SiO₂ (6%) and PMDA-ODA/SiO₂ (42%). The dots represent concentrations of Si atoms.

Table II. Thermal Analysis of Polymers

polym	TGA, ^a °C	T _g , ^b °C
PMDA-ODA	551	346
PMDA-ODA/SiO ₂ (6%)	587	360
PMDA-ODA/SiO ₂ (42%)	564	
BTDA-ODA	545	361
BTDA-ODA/TiO ₂ (2%)	520	
BTDA-ODA/TiO ₂ (12%)		298

^a 10% loss in weight of polymer. ^b From DSC experiments.

ment.⁹ To compensate for this, approximately 1.3 mol of water (per mole of Si(OEt)₄), together with a trace of HCl, was added to the system prior to thermal curing.¹⁰ As Table I shows, this resulted in almost complete retention of the silicon dopant in the polymers.

The presence of dopants in the polymer matrix did not have a dramatic effect on their thermal properties (Table II). Thermogravimetric analysis in N₂ indicated that the polymer decomposition temperature, corresponding to 10% weight loss of the sample, decreased upon doping with TiO₂. On the other hand, unlike previously reported metal oxide containing polyimides,¹¹ the decomposition temperature was found to increase upon the addition of SiO₂. The glass transition temperatures, T_g, as revealed by DSC experiments, also showed a similar trend. However, since polyimides do not display a sharp glass transition point, the values reported in Table II are of limited accuracy.

The energy dispersive X-ray analysis (EDAX) of the surfaces of the doped polymer films showed intense Ti and Si peaks on both the atmosphere and the substrate sides. An X-ray dot mapping of Si on the atmosphere sides of both PMDA-ODA/SiO₂ (6%) and PMDA-ODA/Si (42%) revealed a uniform distribution of silicon throughout the surface of the films (Figure 4). The scanning electron microscopy (SEM) of the titanium containing polymers showed uniform surfaces with no apparent microstructure, on both the atmosphere and the substrate sides of the films. No titanium-containing aggregates were observed by SEM even at a magnification of 60 000. In the case of the silicon-containing polymers, similar results were obtained for up to 32% SiO₂ concentration. At a silica concentration of 42%, however, the scanning electron microgram of PMDA-ODA/Si showed a uniform distri-

bution of spherically shaped silica particles, approximately 1 μm in size, on both the atmosphere and the substrate sides of the film (Figure 5). Careful investigation of the surface of these films revealed that most of these clusters were covered with a very thin layer of the polymer on the immediate surface of the film. The areas where this covering was absent appeared to be connected by microcracks on the polymer surface as confirmed by SEM in a back-scattering mode. As Figure 5 shows, a SEM of the film looking "edge-on" also revealed a uniform distribution of the silica clusters in the bulk of the film. Clearly, in contrast to most previous reports on polyimides doped with metal compounds,⁸ no migration of the metallic species to the film surface had occurred (also see SIMS results).

Further characterization of both the titanium and the silicon species present in the BTDA-ODA and PMDA-ODA polymeric matrices was achieved by X-ray photoelectron spectroscopy (XPS). XPS of the polymer films obtained at a takeoff angle of 90° for maximum sampling depth showed well-defined Ti(2p) and Si(2p) photopeaks on the atmosphere sides of the films. In the case of the BTDA-ODA/TiO₂, the Ti(2p_{3/2}) peak was observed at a binding energy of 458.40 eV and corresponded to the presence of TiO₂¹² (Figure 6). The O(1s) photopeak at 532 eV also suggested the presence of metal oxides.¹³ The Si(2p_{3/2}) photopeak in PMDA-ODA/SiO₂ was at 102.60 eV and corresponded to SiO₂¹⁴ (Figure 7).

The concentration gradient of titanium in BTDA-ODA/TiO₂ film was studied by secondary ion mass spectroscopy (SIMS). A semiquantitative depth profiling from the atmosphere side of the films indicated that the concentration of the titanium species increased on going from the surface to the bulk and then leveled off (Figure 8). This result is in sharp contrast to the previous reports where the migration of the dopant species from the bulk to the surface of the polymers was often observed⁸ (vide infra).

To probe the internal structure of the polymers, ultramicrotomed cross sections of the polymeric films were examined by transmission electron microscopy (TEM). A trend similar to that observed with SEM was evident. In the case of BTDA-ODA/TiO₂, the bulk of the film was found to be perfectly homogeneous, and no titanium-

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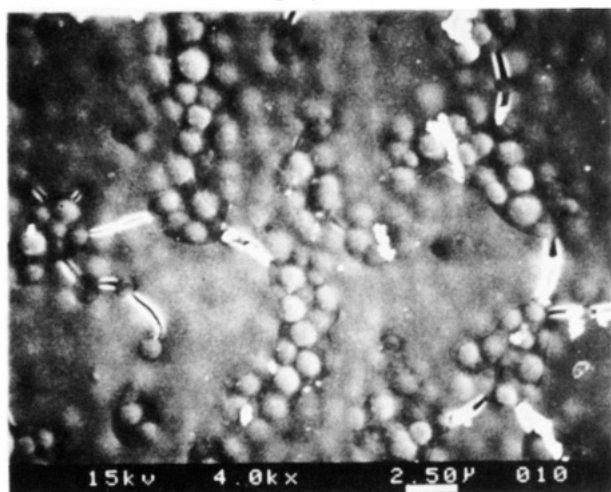
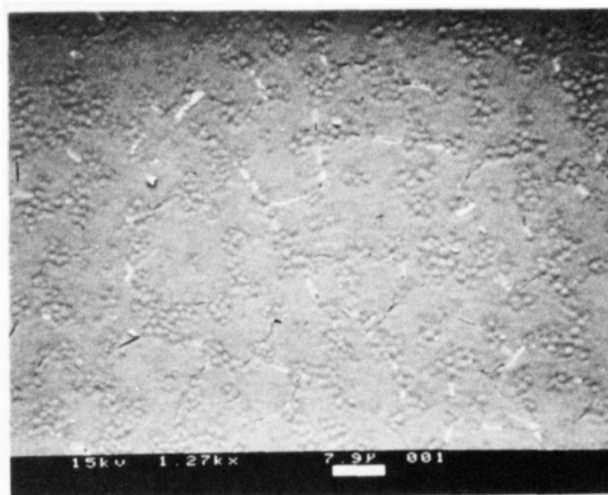
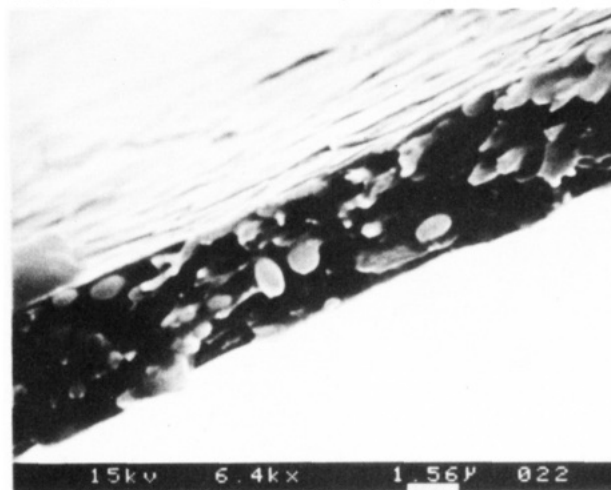
TOP PMDA/ODA/SiO₂ (42%)TOP PMDA/ODA/SiO₂ (42%) WITH BACK-SCATTERINGEDGE ON PMDA/ODA/SiO₂ (42%)

Figure 5. Scanning electron micrographs of PMDA-ODA/SiO₂ (42%).

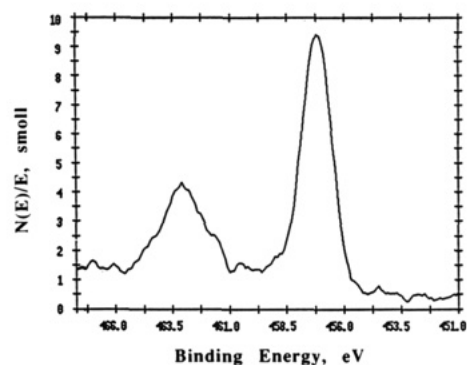


Figure 6. Titanium 2p_{1/2,3/2} photopeak region of the atmosphere side of BTDA-ODA/TiO₂.

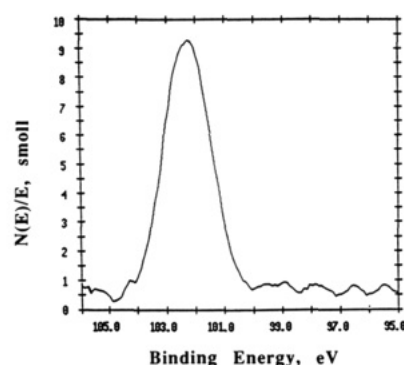


Figure 7. Silicon 2p_{3/2} photopeak region of the atmosphere side of PMDA-ODA/SiO₂.

containing species was detected. In the case of PMDA-ODA/SiO₂, up to a silica content of 32%, the bulk of the film was found to be similar to the titanium-containing polymer. The transmission electron microgram of the cross section of the PMDA-ODA/SiO₂ (42%), however, revealed a uniform distribution of spherically shaped silica particles, 1 µm in size, throughout the bulk of the film. Thus, except for PMDA-ODA/SiO₂ (42%), both SEM and TEM indicate that the size of the oxide particles present in the polymeric matrices was less than 1–1.5 nm, the resolution limit of the instruments.

Finally, to test the concept of “site isolation” leading to the formation of nanoclusters, PMDA-ODA/SiO₂ (12%) films were made by using [–Si(OEt)₂O–]_n (viscosity = 14–16 cSt at 25 °C) rather than Si(OEt)₄ as the silica precursor. Both SEM and TEM of the films revealed a uniform distribution of spherically shaped silica particles, approximately 2 µm in size, throughout the surface and the bulk (Figure 9). Note that particles of size 1–1.5 nm or greater were not observed in PMDA-ODA/SiO₂ films containing up to 32% SiO₂ when Si(OEt)₄ was used as the precursor. This indicates that particles were being formed

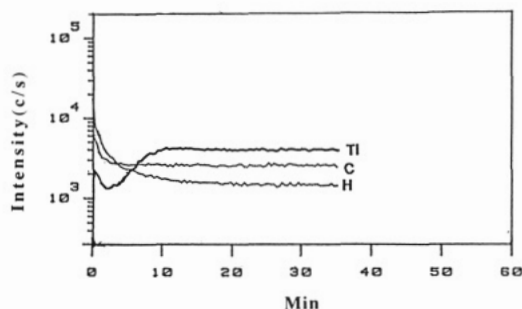


Figure 8. Depth profile of BTDA-ODA/TiO₂ film (Ti, C, H) by secondary ion mass spectroscopy.

in all cases, but with the smaller silica precursor nanoclusters resulted since site isolation prevented agglomeration to larger particles. If, on the other hand, a polymeric silicon precursor is used, large particles are expected despite site isolation.

Discussion

The spectroscopic studies on the doped polyimide films indicate the formation of homogeneous dispersion of SiO₂ or TiO₂ nanoclusters (size <1.5 nm) in the polymers. Remarkably, transparent, flexible, free-standing films were obtained even with a high concentration of dopant (e.g., with up to 32% SiO₂ content). These composite materials differ in two respects from previously synthesized metal oxide containing polyimides.⁸ The latter materials usually exhibit a nonhomogeneous distribution of the oxide particles with markedly higher concentration at or near the polymer surface. In addition, large particles with size >100 nm are usually present. We ascribe this difference to our

use of the "site isolation" technique. The alkoxides of silicon and titanium are known to react with carboxylic acids, leading to the replacement of one or more alkoxides by carboxylate groups.⁹ Thus, it is reasonable to expect that the silicon and titanium precursors will bind to the polyamic acid (cf. eq 1). Hydrolysis does not begin to occur until the thermal curing step when water is released as a result of ring closure (Figure 2). Since the hydrolysis of the carboxylate fragment is slow,⁹ the metal precursors will remain bound to the polyamic acid until all the alkoxide groups have been hydrolyzed off. Once the oxide particles are formed, they will, for the most part, continue to remain site isolated due to the relative rigidity of the polyamide matrix. The coordination of the polyimide carbonyl groups to the metal centers on the surface of the particles may also play a role in preventing cluster mobility. Thus, the "site isolation" strategy that we have adopted prevents significant agglomeration of the metal centers at every stage of the synthetic procedure. Note that there is an upper limit for the dopant concentration beyond which the strategy fails. For example, 1- μ m size particles were formed when SiO₂ concentration reached 42% in PMDA-ODA films.

Finally, because of slow hydrolysis rates for Si(OEt)₄ (compared to Ti(OEt)₄),⁹ significant loss of silicon through the volatilization of the precursor was observed during the thermal curing step. However, this could be effectively prevented by the addition of water and a trace of acid to the system prior to thermal curing.

Experimental Section

General Considerations. Unless otherwise noted, all manipulations were performed in a N₂-filled glovebox where all

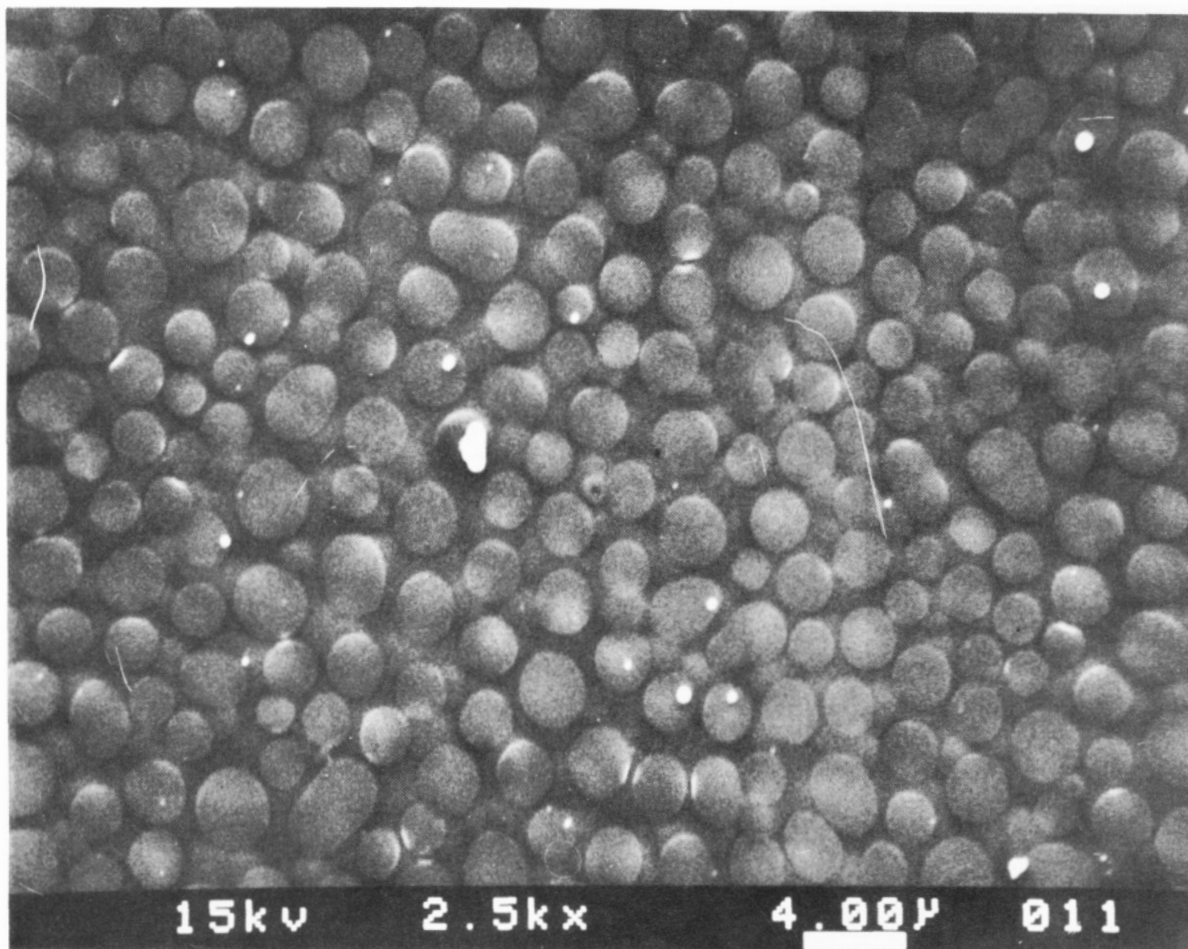


Figure 9. Scanning electron micrograph of PMDA-ODA/SiO₂ (12%) made from poly(diethoxysiloxane) precursor.

reagents and solvents were stored. Standard techniques were used for all Schlenk line and vacuum line manipulations.

The monomers used to synthesize the polyimides were 1,2,4,5-benzenetetracarboxylic acid dianhydride (PMDA), 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA), and 4,4'-oxydianiline (ODA). All the monomers were obtained from Aldrich Chemicals. The chemical structures of the monomers are shown in Figure 1. PMDA and BTDA were purified by sublimation at 200 and 150 °C under 10^{-3} mmHg, respectively. ODA was also purified by sublimation at 150 °C under 10^{-3} mmHg. Titanium and silicon tetraethoxides were obtained from Aldrich Chemicals and were used without any further purifications. Poly(diethoxysiloxane) (viscosity = 14–16 cSt at 25 °C) was obtained from Petrarch Systems. All chemicals, once purified, were stored in a N_2 -filled glovebox. Anhydrous *N*-methylpyrrolidinone (NMP) was obtained from Aldrich Chemicals and was stored under nitrogen.

Synthesis of Polymer Precursors. The polymer precursor, poly(amic acid), was synthesized by the reaction of the appropriate dianhydride and the diamine in NMP (10–15% solids).

In a typical synthesis, the diamine, ODA (1.0 g, 0.005 mol), was taken in a 50-mL glass flask, and the appropriate amount of the solvent (NMP) was added to it. The dianhydride, PMDA (1.079 g, 0.00495 mol), was then added to the solution after complete dissolution of the diamine. The mixture was stirred mechanically for 10–12 h to form a golden-yellow poly(amic acid) solution.

In a typical synthesis of the precursor to the titanium containing polymers, a 50-mL round-bottom flask was charged with ODA (1.0 g, 0.005 mol), and the appropriate amount of the solvent (NMP) was added to it. The titanium precursor, $Ti(OEt)_4$ (1.14 g, 0.005 mol), was added to this solution after the complete dissolution of the diamine. BTDA (1.594 g, 0.0049 mol) was then added to this solution, and the mixture was then stirred mechanically for 12 h to form a golden-yellow titanium precursor/poly(amic acid) solution.

In a typical synthesis of the precursors to the silicon-containing polymers, a 50-mL round-bottom flask was charged with ODA (1.0 g, 0.005 mol), and the appropriate amount of the solvent (NMP) was added to it. After the complete dissolution of the diamine, the silicon precursor $Si(OEt)_4$ (5.2 g, 0.025 mol) was added to it. PMDA (1.079 g, 0.00495 mol) was then added to this solution, and the mixture was stirred for 8 h. At this point, distilled water (0.585 mL, 0.0325 mol) and 3 drops of dilute HCl were added to the solution, and the mixture was stirred again for 6 h to give a homogeneous golden-yellow silicon precursor/poly(amic acid) solution.

Polymer Curing and Film Preparation. The polymer films were prepared by casting either poly(amic acid) solution or the ceramic precursor/poly(amic acid) solution on a glass plate under

a dust-free N_2 atmosphere. All glass plates were cleaned by ultrasonication in hexane and then by washing with doubly deionized water. The polymers were thermally cured by heating under dry nitrogen at 100 °C for 1 h, 150 °C for 1 h, 200 °C for 1 h, and finally 300 °C for 1–2 h. After cooling to room temperature, the high quality free-standing films were easily removed by soaking them in deionized water and peeling off with a razor blade. All the polymer films were finally cleaned by ultrasonication in acetone and hexane. They were then dried in a vacuum oven for 30 min at 140 °C.

Characterization of Polymers. All elemental analysis were done at Galbraith Laboratories, Knoxville, TN.

A Du Pont Thermal Analyst 2100 system was used for the thermogravimetric analysis. The samples were heated at the rate of 10 °C/min from room temperature to 1000 °C under a flow of dry N_2 at 10 mL/min. Differential scanning calorimetric experiments were carried on a Perkin-Elmer DSC 7 heated at a rate of 20 °C/min from room temperature to 450 °C under N_2 .

Scanning electron micrograms (SEM) were taken on a International Scientific Instruments Model DS130 scanning electron microscope. All samples were gold coated, mounted on aluminum mounts with silver cement. Energy dispersive X-ray analysis and X-ray dot mapping were done with a Kevex 8000 system.

Transmission electron micrograms (TEM) were obtained by using a Philips 300 transmission electron microscope. Samples were prepared by embedding small strips of polymer films in Spurr media,¹⁵ which was then polymerized at 70 °C overnight. Samples were sectioned to 500 Å by using a dry glass knife mounted on a LKB Ultratome III. Care was taken to cut the cross sections perfectly straight so as not to have blurred edges on the polymer film strips. The thin sections were placed on a 200-mesh copper grid for analysis.

X-ray photoelectron spectra were obtained with a Perkin-Elmer PHI Model 5000LS ESCA system. A monochromatic X-ray source with an aluminum anode (Al $K\alpha$ = 1486.7 eV) run at 600 W (15 kV and 40 mA) was used. The analysis area was set at 1.1 mm, and the takeoff angles used were 43° and 90°. All binding energies were referenced to the aromatic C(1s) photopeak at 284.6 eV.

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Registry No. (PMDA)(ODA) (copolymer), 25038-81-7; (PMDA)(ODA) (SRU), 25036-53-7; (BTDA)(ODA) (copolymer), 24980-39-0; (BTDA)(ODA) (SRU), 24991-11-5; SiO_2 , 7631-86-9; TiO_2 , 13463-67-7; $Si(OEt)_4$, 78-10-4; $Ti(OEt)_4$, 3087-36-3.

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