Polyimide–Siloxane Hybrid Materials: Influence of Coupling Agents Addition on Microstructure and Properties

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SYNOPSIS

Polyimide–silica hybrid materials were prepared by polycondensation, polyimidization, and sol–gel coreactions. Several aminoalkoxysilane precursors providing a chemical bonding between the inorganic and the organic phase were used. During the synthesis, the molecular structure of the materials prepared with these precursors were followed at various steps by ^{29}Si-NMR (nuclear magnetic resonance). The final materials were characterized at the macroscopic level by thermogravimetric analysis and scanning electron microscopy and at the molecular level by infrared spectrometry and ^{29}Si-MAS–NMR spectroscopy. It has been demonstrated that the properties of the organic sidegroups of the bonding agent are determinent on the properties of the final material. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The combination of inorganic and organic or bioactive components in a hybrid material makes accessible a large environment area of materials science. These materials[1] have promising developments in a wide range of applications, like biosensors, hard coatings, and new rubbery solids.

Most organic–inorganic hybrid composites are prepared via the sol–gel process.[2,3] The formation of the inorganic backbone is based on a condensation step including the formation of metal/oxygen/metal bonds. The organic part can be introduced by various ways: Organics can be dissolved in the sol and are trapped during the gelation in the porous amorphous gel; an organic can be impregnated into a gel to form a nanocomposite material; and finally, a chemical bond can be formed between an organic and residual hydroxide groups.

To improve the temperature resistance of hybrid materials, high-temperature polymers can be used as the organic phase. Because of the high thermal stability of polyimides, numerous studies have been carried out on the preparation of polyimide siloxane materials. These materials are prepared following different techniques. Copolymers have been synthesized using coreaction of polymethyldisiloxane (PDMS) and imide precursors.[4-11] The sol–gel process has been used to prepare polyimide–silica composites where silica particles are dispersed in a polyimide matrix.[12-16] Polyimide–silica materials have been also prepared via sol–gel chemistry using precursors which can provide chemical bonding between the organic and the inorganic phase. The first report of a chemical bond between the polymer and the silica was presented by Spinu et al.[17] Hexamethoxy functionalized polyimide oligomers were hydrolyzed and co-condensed with TMOS (tetramethoxysilane) at elevated temperatures under mild pressure via sol–gel processing. Various proportions of TMOS were introduced in the materials, and the extent of conversion was studied by ^{29}Si solid-state nuclear magnetic resonance (NMR) as a function of the processing temperature. Then Wang et al.[18-20] used commercial silicon alkoxides containing amino and chloro groups which provide the bonding with the polyimide. The bonding between the polymer and the silica phases was achieved using aminophenyltrimethoxysilane, (aminoethylaminomethyl)phenethyltrimethoxysilane, and 1-trimethoxysilyl-2-(m,p-chloromethyl)phenylethane. These bonding agents can undergo hydrolysis and polycondensation along with the tetramethoxysilane to form silica. The reactions were carried out in the polyamic acid, which

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was then cyclized at high temperatures. Composition of these materials was varied by changing the linear polymer chain length and relative amount of tetramethoxysilane. The thermal stability of these hybrid materials was measured by means of thermogravimetric analysis (TGA). Adding small amounts of these bonding agents was found to improve the moduli and strengths of these materials. Silica clusters were also found by scanning electron microscopy (SEM), and the addition of bonding agent was found to induce a particle size reduction.

This article will present the preparation by polycondensation, polyimidization, and sol–gel coreaction of hybrid polyimide–silica composites with a chemical bonding between the polymer and the oxide phase provided by organoalkoxysilanes. Composite polyimide–silica materials consisting of silica particles homogeneously dispersed in a polyimide matrix have been already prepared using the sol–gel process, and correlation between the synthesis parameters and the final microstructure has been pointed out.[21] In this work, several precursors able to provide a bonding between the inorganic and the organic phase have been used. These various bonding agents present tailored thermally stable or hydrophobic/hydrophilic functions: diaminophenyltetramethyldisiloxane (DAPTMDS, I), aminophenyltrimethoxysilane (APTMOS, II), aminopropyltrimethoxysilane (APrTMOS, III), aminopropylmethyldiethoxysilane (APrMDEOS, IV), and diaminopropyltetramethyldisiloxane (DAPrTMDS, V). The chemical structure of these various precursors is shown in Figure 1. Synthesis with precursors I and V resulted in the formation of hybrid polyimide–siloxane linear chains materials, while synthesis with precursors (II), (III), and (IV) led to the formation of hybrid polyimide–siloxane network materials. Materials obtained with these precursors have been characterized by TGA, infrared (IR) spectrometry, and ^{29}Si-NMR. It has been demonstrated that the functions existing on the bonding agent are determinant on the properties of the final material. Finally, the coating feasability of these various hybrid materials has been tested and observed by SEM.

EXPERIMENTAL

Starting Materials

For the synthesis of DAPTMDS 1,3-diphenyltetramethyldisiloxane [56-33-7] (Hüls America Inc.), acetic anhydrid [108-24-7] (97.5% Prolabo), nitric
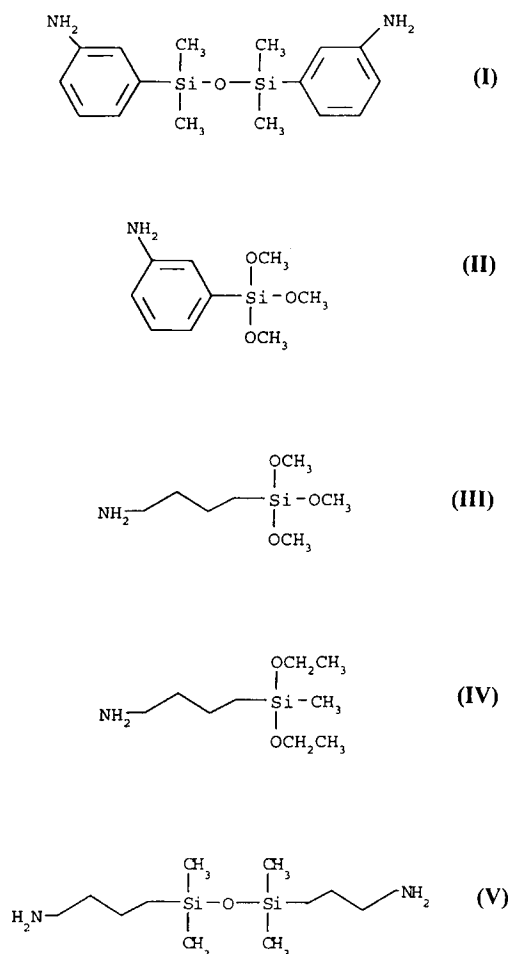

Figure 1 Schematic chemical structure of the different siloxane precursors used for the synthesis of polyimide–siloxane materials DAPTMDS (**I**), APTMOS (**II**), APrTMOS (**III**), APrMDEOS (**IV**), DAPrTMDS (**V**).

acid [7697-37-2] (100%, d = 1.52, Merck), dichloromethane [75-09-2] (99.9%, SDS), ethyl alcohol [64-17-5] (ethanol, 99.8%, SDS), and iron powder [7439-89-6] (98%, Prolabo) have been used as received.

Because of its excellent thermal and chemical stability, we used a typical aromatic polyimide, the poly(4,4-oxydiphenylene pyromellitimide). Its preparation is carried out starting from pyromellitic dianhydride and 4-aminophenyl ether. The monomers 4-aminophenyl ether (4,4'-oxydianiline, ODA, 97%) [101-80-4], 1,2,4,5-benzenetetracarboxylic anhydride (pyromellitic dianhydride, PMDA, 97%) [89-32-7], and anhydrous n,n-dimethylacetamide DMAc [127-19-5] (Aldrich Chemicals) were stored under argon.

The coupling agents APTMOS [33976-43-1], APrTMOS [13822-56-3], APrMDEOS [3179-76-8],

and 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (diaminopropyltetramethyldisiloxane, DAPrTMDS) [2469-55-8] (Hüls America Inc.) have been used as received and stored under argon. The silica network builder, tetramethoxysilane (TMOS) [681-84-5] (Hüls America Inc.), was used as received. Deionized water (18 MΩ) was used for their hydrolysis. The ^{29}Si-NMR spectra recorded on TMOS, APrTMOS, and APrMDEOS pure alkoxides and DAPrTMDS contain a single peak at −78.6, −41.77, −5.8, and 3.8 ppm, respectively, showing the absence of any hydrolyzed or modified species. Concerning the APTMOS precursor, two peaks located at −55.1 and −54.44 ppm are present in the ^{29}Si-NMR spectrum, showing a slight hydrolysis of the precursor. Unfortunately, it has not been possible to find a nonhydrolyzed APTMOS precursor.

Characterization Techniques

Organosiloxane hydrolysis and condensation kinetics have been followed with ^{29}Si-NMR spectra recorded on a Bruker 250 spectrometer operating at 49.695 MHz. The spectra have been obtained with a pulse of 2 μs, a repetition time of 20 s, and 60 accumulations. Molecular structure of the solid materials was determined from 59.62 MHz ^{29}Si-NMR spectra recorded on a Bruker MSL 300 spectrometer by using the magic angle spinning (MAS) technique. The spectra were obtained with a pulse of 5.8 μs (pulse angle 60°) and repetition time of 20 s, and 1500 transients were accumulated before Fourier transformation. The samples were put in an alumina rotor, which was rotated at 5 kHz. These conditions have been checked for quantitative analysis of the spectra. The spectra width was 15 kHz; 16K of data points were used. All samples were kept at a constant temperature of 21°C throughout the experiments. The chemical shifts are given with reference to tetramethylsilane (TMS).

Classical notation, D and T, was used for the different silicate species depending on the number of carbon and oxygen bridging atoms; i indices represent the number of oxo bridges. D^i is used for species which have two organic sidegroups and i siloxane bridges (i = 0, 1 or 2). In the same manner, T^i denotes species which have one organic sidegroup and i siloxane bonds. Literature references[22-24] provide information on the average chemical shift ranges of D^1, D^2, T^1, T^2, and T^3 species. The relative proportions of the D^i (or T^i) species were calculated on the basis of the experimental spectra.

IR measurements were obtained on KBr compacted powder or directly on films with a FTIR Ni-

colet Impact 400D spectrometer. TGA was performed on a Setaram TG 85 apparatus using a 250°C/h heating rate in air. SEMs were obtained from a Hitachi S-4500 microscope.

Synthesis of Diaminophenyltetramethyldisiloxane

The DAPTMDS (I) was synthetized following the synthetic procedure described by Bonnet et al.[25] Figure 2 shows the preparation starting from 1,3-diphenyltetramethyldisiloxane. This synthesis is divided into two steps: (1) a nitration of the diphenyltetramethyldisiloxane with nitric acid in the presence of acetic anhydride, and (2) an amination, which leads to the diaminophenyltetramethyldisiloxane.

During all the nitration, the reactor is maintained in a −15°C--−25°C temperature range by means of a mixture of liquid nitrogen ethanol. In a 250-mL two-necked flask, 17 mL of nitric acid are added dropwise to 25 mL of acetic anhydrid under stirring and anhydrous argon atmosphere. The solution is then stirred at −20°C for 1 h, giving a limpid and incolore solution. Then 20 g of 1,3-diphenyltetra-
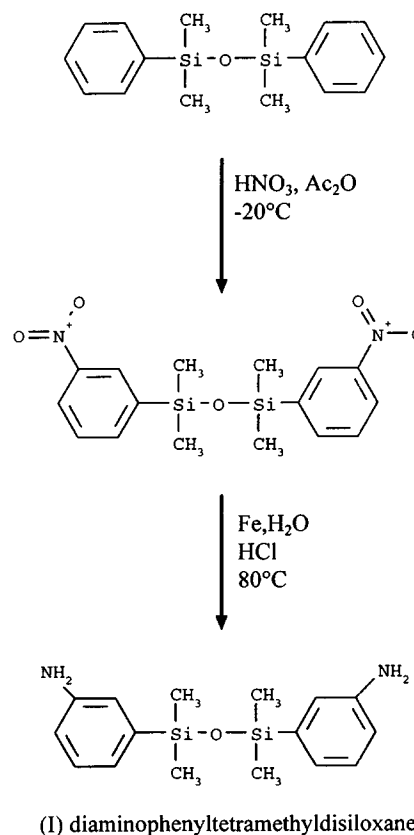

(I) diaminophenyltetramethyldisiloxane

Figure 2 Preparation of diaminophenyltetramethyldisiloxane DAPTMDS (I).

methyldisiloxane diluted in 100 mL of dichloromethane is introduced dropwise in the solution. The addition takes about 2 h, and the resulting mixture is stirred for 1 h, giving a clear yellow solution. One hundred milliliters of deionized water (18 MΩ) is then added to the solution, giving a two-phase mixture. The dichloromethane phase is then washed with water until neutrality of the aqueous phase and removed. This phase is then dried and the dichloromethane is eliminated under vacuum. The final product is a viscous clear yellow solution of m-nitrophenyltetramethyldisiloxane.

For the amination, a solution of 20 g of m-nitrophenyltetramethyldisiloxane is mixed with 100 mL of ethanol and 100 mL of deionised water (18 MΩ). Forty grams of iron powder are added to the solution under stirring, and the resulting mixture is heated at 80°C. One milliliter of chloride acid is then added and the mixture is maintained at 80°C under reflux for 4 h. The iron powder is filtrated and the diaminophenyltetramethyldisiloxane is extracted by the dichloromethane. The product is purified on carbon black and dried on sodium sulfate. The solvent is then eliminated under vacuum giving a brown oil characteristic of the diaminophenyltetramethyldisiloxane.

Nitration and amination products have been characterized by proton NMR and microanalysis studies. These results and comparison of experimental to theoretical data are reported in Table I. NMR spectroscopy analysis includes peaks integration ratios of methyl groups (near 0 ppm) on phenyl groups (7–8 ppm) and phenyl sidegroups on amino groups (4 ppm). The difference between theoretical and experimental phenyl/amino values shows that the amination is not complete. This is confirmed by the presence of additional peaks on the ^{1}H-NMR spectra around 7.5–8 ppm, corresponding to nitro species. There is also a difference between theoretical and experimental methyl/phenyl values. This shows a lack of methyl sidegroups directly bonded to the silicon and will be explained further.

The final product has been characterized by ^{29}Si-NMR. The spectrum shows the presence of two types of species located in the regions of monomers (0 to −2) ppm) and dimers (−20 ppm) in proportions 63 to 37%, respectively. Moreover, several peaks are present in each region. They may correspond to various isomers having the amino substituents in different positions (ortho, meta, or para). The lack of methyl sidegroups directly bonded to the silicon is explained by the presence of dimers. Energy bond data show also that Si — Me bonds are more likely broken than Si — phenyl bonds. Thus, during the

Table I Experimental Data of Intermediate Products Obtained for Synthesis of DAPrTMDS

Compounds	Yield	^{1}H-NMR Chemical Shift (ppm)	Organic Sidegroups Area Ratio	Microanalysis
1,3-Diphenyltetramethyl-disiloxane		0.3 (12H, s, Si—CH₃) 7.34–7.52 (10H, m, phenyl)	H(CH₃)/H(Phenyl)$_{th}$ = 1.2 H(CH₃)/H(Phenyl)$_{exp}$ = 1.2	
m-Nitrophenyltetramethyl-disiloxane	58%	0.09–0.5 (12H, m, Si—CH₃) 5.29 (1.44H, s, CH₂Cl₂) 7.53–8.24 (7.9H, m, phenyl)	H(CH₃)/H(Phenyl)$_{th}$ = 1.5 H(CH₃)/H(Phenyl)$_{exp}$ = 1.52	C$_{th}$ = 51.1 H$_{th}$ = 5.3 N$_{th}$ = 7.5 C$_{exp}$ = 49.3 H$_{exp}$ = 5.3 N$_{exp}$ = 8.1
DAPrTMDS	45%	0.1–0.54 (11.3H, m, Si—CH₃) 3.59 (3.8H, s, NH₂) 6.7–7.22 (7.3H, m, phenyl) 7.53–8.24 (0.7H, m, phenyl)	H(CH₃)/H(Phenyl)$_{th}$ = 1.5 H(CH₃)/H(Phenyl)$_{exp}$ = 1.4 H(Phenyl)/H(amino)$_{th}$ = 2 H(Phenyl)/H(amino)$_{exp}$ = 2.1	C$_{th}$ = 60.7 H$_{th}$ = 7.6 N$_{th}$ = 8.9 C$_{exp}$ = 54.9 H$_{exp}$ = 7.8 N$_{exp}$ = 8.2

X_{th} and X_{exp} represent the theoretical and experimental proportion, respectively, of the element X.

synthesis, Si—Me bonds may break due to the strong synthesis conditions, and these Si—Me bonds may be replaced by siloxane bonds.

RESULTS

Preparation of Polyimide Silica Hybrid Materials

Preparation of Polyimide Siloxane Linear Chains Material with Precursors I and V

Figure 3 shows the preparation starting from PMDA, ODA, and precursor I. This preparation can be divided into two steps: the polyamic acid preparation (polymerization) and the polyimide preparation (imidization).

Two polyamic acids have been synthesized using precursor I. One is prepared by reaction of the dianhydride with precursor I in DMAc without adding ODA in the mixture; this material will be called I 100%. The second is prepared by using a molar equal amount of precursor I and ODA; this will be named I 50%. In a 100-mL three-necked flask, DAPTMDS ODA (optional), and 30 mL of DMAc

are mixed at room temperature for 30 min under argon atmosphere. A stochiometric amount of solid PMDA with 20 mL of DMAc are added to this solution and stirred at room temperature for 3 h under argon atmosphere. The polyamic acid is then precipitated in ether.

Similar preparation has been used with precursor V. When only PMDA is added in the mixture (precursor V 100%), the exothermic reaction usually observed with precursor I does not occur and no precipitate is obtained in ether. For material obtained with addition of ODA (V 50%), a reaction is observed giving a yellow solid after precipitation. Table II provides the composition, aspect, and yield of hybrid polymers synthetized after precipitation in ether. These amic solutions obtained with precursor I (I, 100% and I, 50% and V 50%) have been characterized before imidization by means of ^{29}Si-NMR. ^{29}Si-NMR spectrum recorded on the V 50% polyamic acid does not show any peak. As few percent of silicon can be detected by NMR; this polyamic acid solution contains at the very maximum a few percent of silicon species. As already observed in the polyamic acid solution (V 100%),
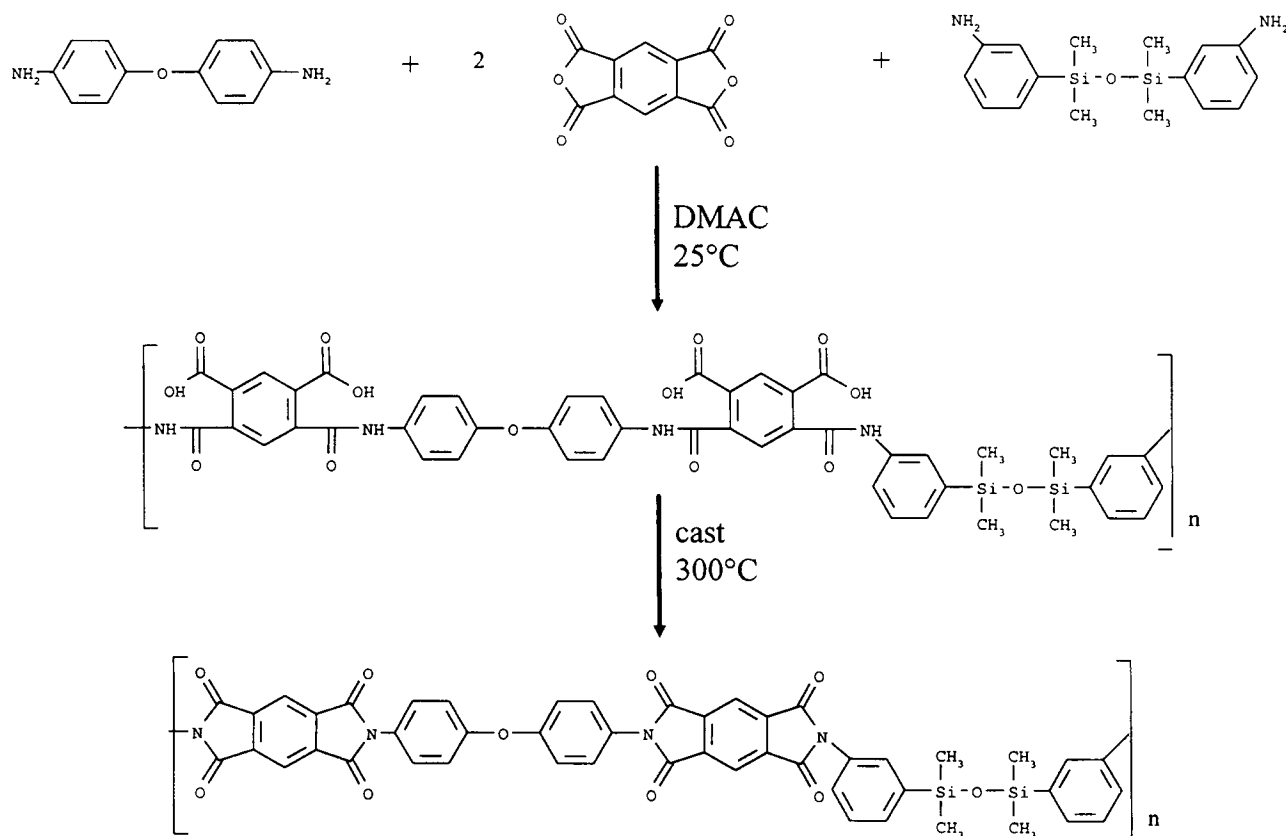

Figure 3 Preparation of polyimide siloxane linear chains materials starting from DAPTMDS (I).

Table II   Composition, Aspect, and Yield of Various Polyamic Acids

| Compounds | ASi/PMDA (mol %) | Composition in g (mol) | | | Aspect after Precipitation | Yield |
		ASi	ODA	PMDA		
PAA ODA–PMDA	0	0	4 (0.02)	4.38 (0.02)	White solid	80%
PAA–H(I 50%)	50	3.16 (0.01)	2 (0.01)	4.38 (0.02)	Brown oil	78%
PAA–H(I 100%)	100	6.33 (0.02)	0	4.38 (0.02)	Brown oil	81%
PAA–H(V 50%)	50	2.48 (0.01)	2 (0.01)	4.38 (0.02)	Yellow solid	58%
PAA–H(V 100%)	100	4.97 (0.02)	0	4.38 (0.02)	No reaction	0%

ASi, diaminoalkylalkoxysilane; PAA, polyamic acid.

most quantity of precursor V does not react with the PMDA and is eliminated during the precipitation step. Thus, during the synthesis, a few percent of hybrid materials are formed at best; the major part of the material results in a PMDA–ODA reaction. This interpretation is confirmed by the small yield of the V 50% polyamic acid synthesis, which corresponds to elimination of the precursor V, to the PMDA–ODA reaction yield. Spectra obtained on I 50% and I 100% are similar to the spectrum obtained on precursor I, showing the presence of monomers (M specie) and dimers (D specie). The proportion of dimers does not change compared to pure precursor, showing that the addition of PMDA and ODA does not affect the siloxane bonds environment.

For the imidization, DMAc is first added to the polyamic acid substance to form a homogeneous solution after stirring for 60 min at room temperature. This solution is then cast onto a glass plate by the tape-casting technique for film obtainment or onto alumina support (provided by VITO Company) by the spin-coating technique. Polyimide silica hybrid materials are obtained by heating the PAA hybrid stepwise (60°C for 6 h and 100°C for 2 h at atmospheric pressure, and finally at 230°C for 10 min and 300°C for 3 h under vacuum).

Preparation of Polyimide–Siloxane Network Materials Using Precursors II, III, and IV

Figure 4 shows the preparation starting from pyromellitic dianhydride (PMDA) and monoaminoalkylalkoxysilane II, III, or IV. This preparation can be divided into two steps: the amic acid solution preparation and the silica network and polyimide coreaction.

The amic acid solution is synthetized by condensation of 0.02 mol of dianhydride with 0.04 mol of monoaminoalkylalkoxysilane in 50 cm³ of DMAc under argon, giving weight solids solution concentration between 25 and 28%. In a 100-mL three-necked flask, 4.38g (0.02 mol) of PMDA and 50 mL of DMAc are stirred at room temperature for 30 min under dry argon atmosphere. Then 0.04 mol of monoaminoalkylalkoxysilane are added and stirred at room temperature for 3 h under argon atmosphere. Homogeneous brown, yellow pale, and yellow amic acid solutions are then obtained with the monoaminoalkylalkoxysilane II, III, and IV, respectively. The spectra obtained on these amic acid solutions by ^{29}Si-NMR are presented on Figure 5. They show the presence of monomeric species located in the chemical shift range of the pure precursors and condensed species containing one siloxane bond for APrTMOS (III) and APrMDEOS (IV) amic acid solutions. No condensed species are observed for amic acid solutions obtained with APTMOS (II). The peaks corresponding to these condensed species are situated around −50 and −13 ppm for amic acid solutions synthetized with APrTMOS and APrMDEOS, respectively.

Deionized water in proportion of 4 mol of water for 1 mol of amic acid is then added to the solution, and this mixture is stirred for a few hours at room temperature. Finally, the polyimide–silica hybrid materials are obtained by casting the hydrolysed amic acid solution onto alumina substrates (provided by VITO Company) and heating the precursor hybrid film with the same heat treatment described earlier [60°C for 6 h, 100°C for 2 h at atmospheric pressure, 230°C for 10 min, and 300°C for 3 h under vacuum].
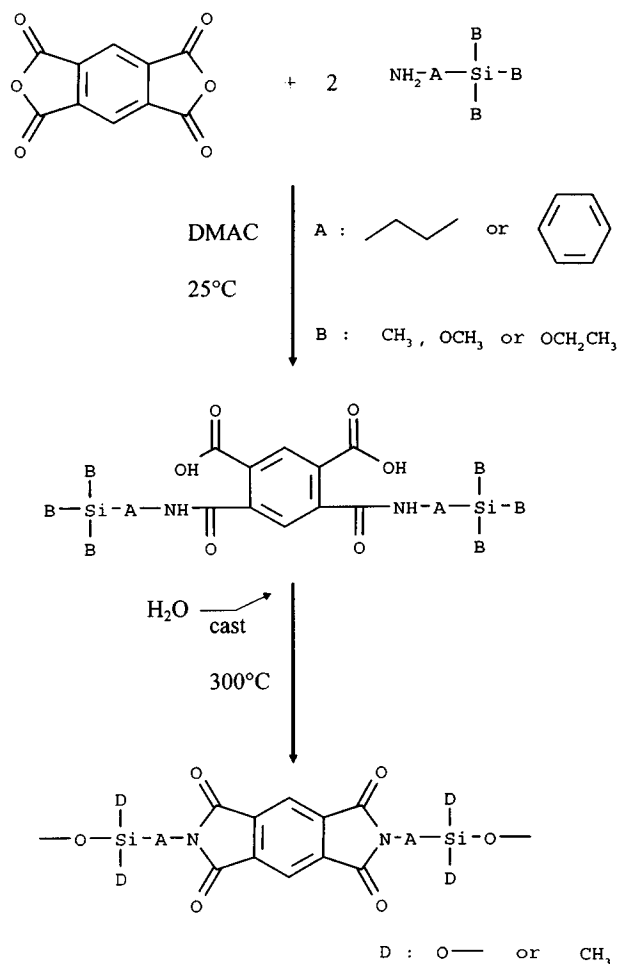
Figure 4 Preparation of polyimide–siloxane network materials starting from monoaminoalkylalkoxysilane APTMOS (II), APrTMOS (III), and APrMDEOS (IV).

Materials Characterization

Figure 6 shows schematic theoretical structure of the final materials: polyimide–siloxane **I, II, III, IV,** and **V**. The hybrids **I** and **V** present only one siloxane group and two methyl groups directly bonded to each silicon atom. Methyl groups should inhibit the formation of bonds, resulting in the formation of linear chains without any crosslinking. On the contrary, hybrid **IV** shows the presence of two siloxane bonds per silicon atom, giving a three-dimensional network material. The presence of three siloxane bonds per silicon atom induces a more crosslinked material for hybrid **II** and hybrid **III**, assuming that condensation occurs completely and that there is no steric hindrance limitation.

²⁹Si-NMR

The molecular structure of these various materials was studied by means of ²⁹Si-NMR. As APTMOS

and APrTMOS differ only by the amino side group, materials obtained with siloxane precursors **II** and **III** (APTMOS and APrTMOS) have been studied more accurately from the hydrolysis–condensation reactions to the final material. The comparison of the reactions between these two precursors enables the understanding of the influence of the siloxane precursor on the final molecular structure. Figures 7 and 8 present spectra recorded on these two amic acid solutions as a function of time. The last spectrum is recorded by MAS–NMR on the final material. The condensation in the APTMOS system is obviously slower than in the APrTMOS system. Although the as-received APTMOS precursor is hydrolyzed, T^1 species appear after 17 h of reaction, while they are already present after a few minutes of hydrolysis in the solution containing the APrTMOS precursor. Thus, as we have seen that the addition of PMDA to the APrTMOS alkoxysilane precursor induces an early condensation, the final solid network should be more condensed when APrTMOS is used as a coupling agent.

A quantitative estimation of the connectivity can be made by calculation of the condensation ratio of
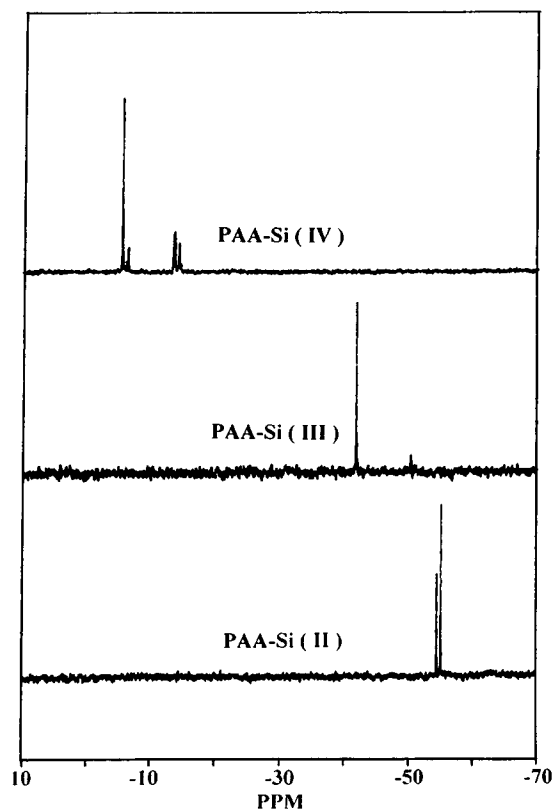

Figure 5 ²⁹Si-NMR spectra obtained on amic acid solution (PAA–Si) obtained with precursors APTMOS (II), APrTMOS (III), APrMDEOS (IV).
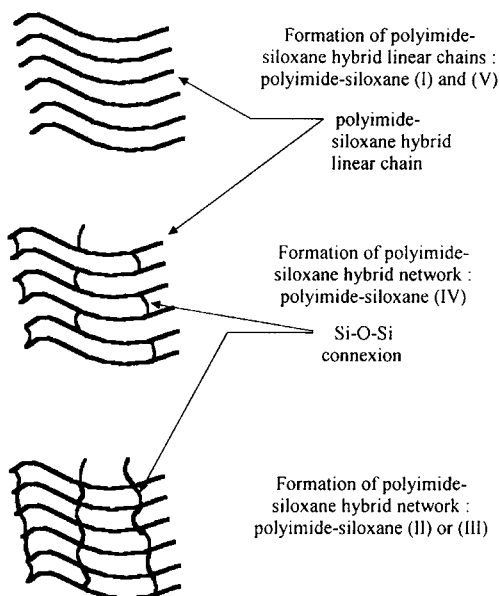
Figure 6 Theoretical schematic structure of polyimide–silicon materials **I, II, III, IV,** and **V.**

these two networks on the basis of MAS-NMR data. This condensation ratio represents the proportion of siloxane bonds over the theoretically possible siloxane connections. The condensation ratios of materials obtained with APrTMOS and APTMOS are equal to 0.84 and 0.63, respectively. These values are further evidence of the higher connectivity of APrTMOS materials. This difference may be explained by the steric hindrance provided by the phenyl sidegroups, which inhibits Si—O—Si bonding.

MAS-NMR spectra have been recorded on all final materials (Fig. 9). Concerning the linear chains materials, the spectrum obtained on final material (**V 50%**) does not show any silicon species, confirming the observation made on the polyamic acid solution. The spectra obtained on materials **I 100%** and **I 50%** are similar to those obtained on the polyamic solutions, with the presence of monomers and dimers in proportions equal to 67% and 33%, respectively. This proportion is identical to that calculated for pure precursor **I.** This shows that, in this material, the thermal treatment and the polymerization do not induce any redistribution in the siloxane network.[26]

The condensation ratio of the APrMDEOS (**IV**) materials has been compared with those calculated on APrTMOS and APTMOS. The condensation ratio of APrMDEOS is equal to 0.98, showing that this material is more condensed than APrTMOS and APTMOS. This increase in reticulation may be

due to the presence of only two alkoxy groups in APrMDEOS. The steric hindrance of three alkoxy groups inhibits the complete condensation of APrTMOS and APTMOS.

IR Spectroscopy

Structural characteristics of pure polyimide and hybrid polyimide–silica material were obtained by IR analysis (Fig. 10). All samples present characteristic bands of imide bonds at 720 cm^{-1}, 1380 cm^{-1}, and 1779 cm^{-1}. All hybrid materials, except hybrid **V,** exhibit a strong broad absorption band around 1000–1100 cm^{-1} characteristic of Si—O—Si bonds. Hybrid **V** presents just a small absorption band in these wave numbers. This confirms the insignificant amount of siloxane bonds present in this material. Concerning network materials, this absorption band is broader in materials **II** and **III** (100 cm^{-1}) than material **IV** (50 cm^{-1}). The narrowing of this band in hybrid **IV** indicates that the silicon environment in this material is more homogeneous than in ma-
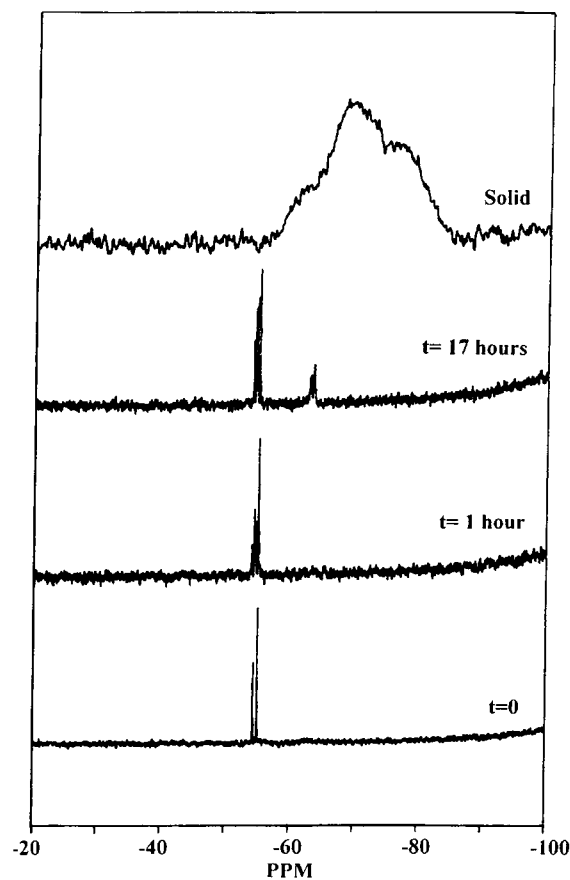

Figure 7 ^{29}Si-NMR spectra recorded during the hydrolysis as a function of time on amic acid solution starting with APTMOS (**II**).
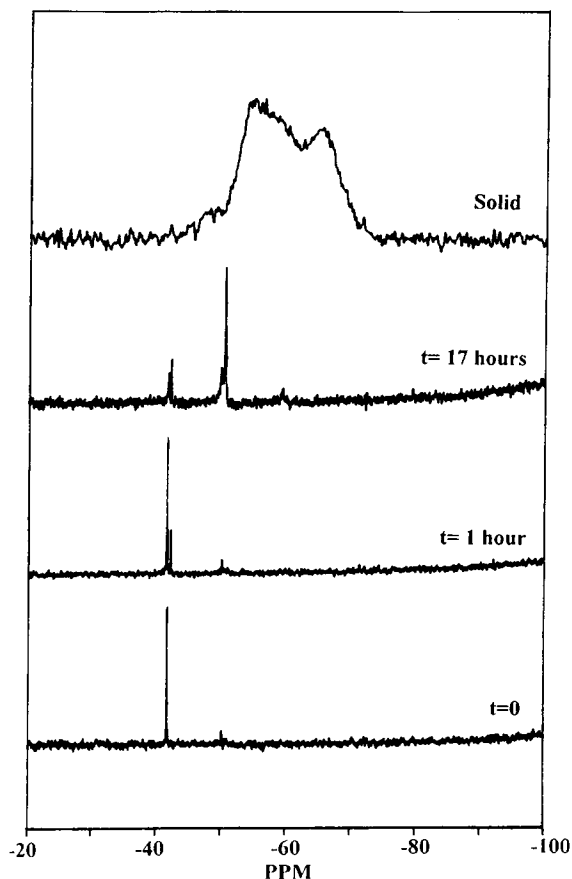
Figure 8 ^{29}Si-NMR spectra recorded during the hydrolysis as a function of time on amic acid solution starting with APrTMOS (III).

terials **II** and **III**. This result is correlated with ^{29}Si MAS–NMR spectra. A majority of D^2 species are present in material **IV**, while no specific condensed specie is in majority in materials **II** and **III**.

Absorption bands in the range 3700–3200 cm^{-1} are characterized by OH stretch band of free or hydrogen-bonded OH. Hybrids polyimide–siloxane **I** and **IV** have no significant IR absorption in this region, whereas all other samples present an important wide band in this region. These two precursors are characterized by the presence of methyl sidegroups linked to the silicon. Thus, the presence of these methyl sidegroups inhibits the formation of OH free or OH linked bonds in the material.

TGA

Thermal decomposition in air is presented in Figure 11. Figure 11(a) shows the difference in thermal properties of chain materials prepared with 100% of precursor **I** and a mixture of 50% of precursor **I** (or **V**) and ODA. Depending on the proportion of pre-

cursor **I** in the material, the decomposition temperature of the materials can be below (400°C) or above (500°C) the decomposition of a pure polyimide. This behavior shows that the introduction of silicon in the network does not improve the thermal stability of the polyimide but is a matter of its proportion in the polymer network. The thermogravimetric curve obtained for material **V 50%** is almost similar to that of a pure polyimide. This behavior is consistent with the results obtained by ^{29}Si-NMR, which showed the absence of silicon in the material.

No significant difference in the thermal behavior is observed between the linear chain and the network materials. The rate of degradation of hybrid polyimide is reduced compared to pure polyimide. This behavior may be attributed to the presence of siloxane bonds in the polymer. The final weight residue at 900°C is a white silica powder. Table III presents the experimental and theoretical (calculated on the assumption that every silicon atom can be converted into silicon oxide) values of silicon oxide obtained on the various polyimide siloxane materials. These
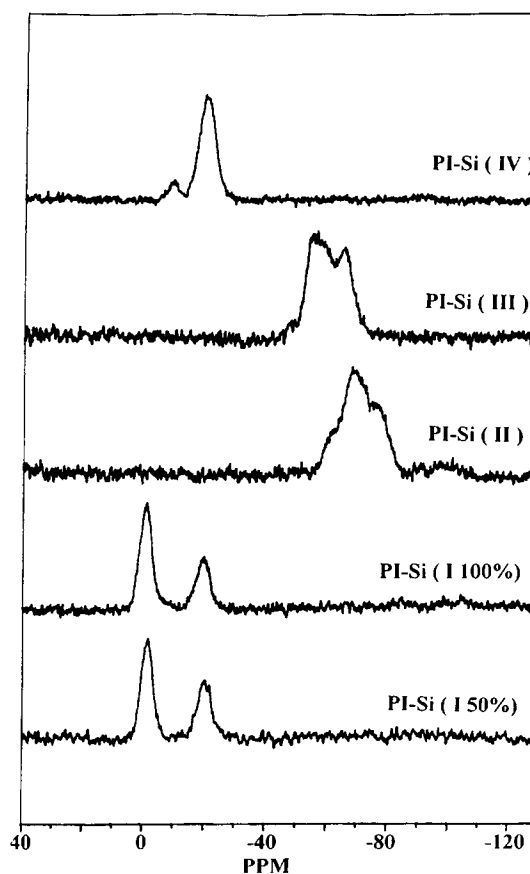

Figure 9 ^{29}Si-MAS-NMR spectra recorded on polyimide–siloxane hybrid materials (PI — Si): **I, 50%, I, 100%, II, III,** and **IV**.
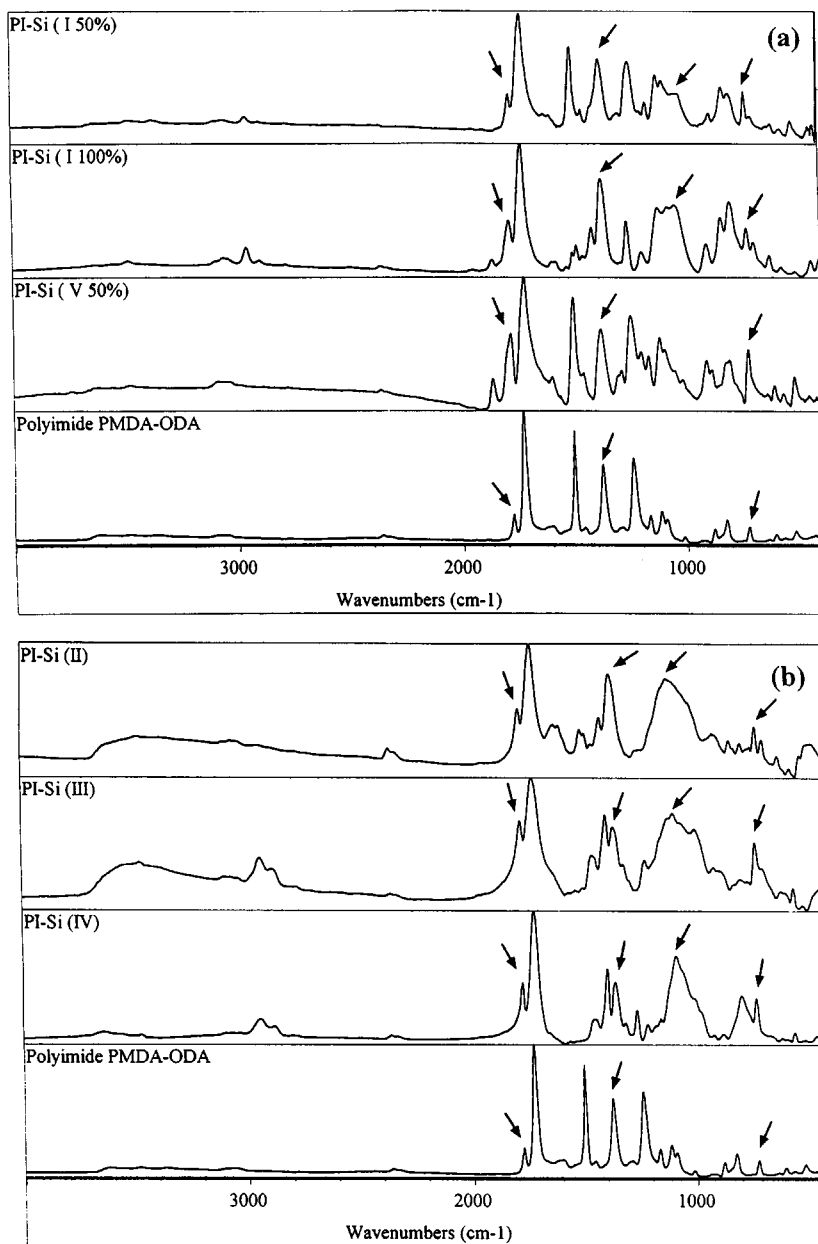
Figure 10   Infrared spectra obtained on various polyimide–siloxane materials (PI — Si).
(a) Polyimide–siloxane linear chains materials, (b) polyimide–siloxane network materials
with precursors **II, III, and IV.**

results show that almost all silicon atoms participate
to the formation of silica. Between 400 and 500°C,
important weight losses are observed for all samples
corresponding to the pyrolysis of organic com-
pounds.

Depending on the sidegroups present on the si-
loxane precursor, differences are observed on the
decomposition temperature [Fig. 11(b)]. For mate-
rials having a propyl group [corresponding to mono-
mers **III** and **IV**], decomposition starts at 400°C

while it occurs around 550°C for polyimide having
a phenyl group (**II**). This behavior is explained by
a dissociation energy of C — C bonds, which is lower
in propyl groups (83–85 kcal at 25°C) than in phenyl
groups (120 kcal at 25°C).

Moreover, in contrast to pure polyimide and hy-
brid polyimide–siloxane **II** and **III**, no weight loss
is observed below 300°C for hybrid polyimide con-
taining methyl groups [hybrid polyimide–siloxane **I**
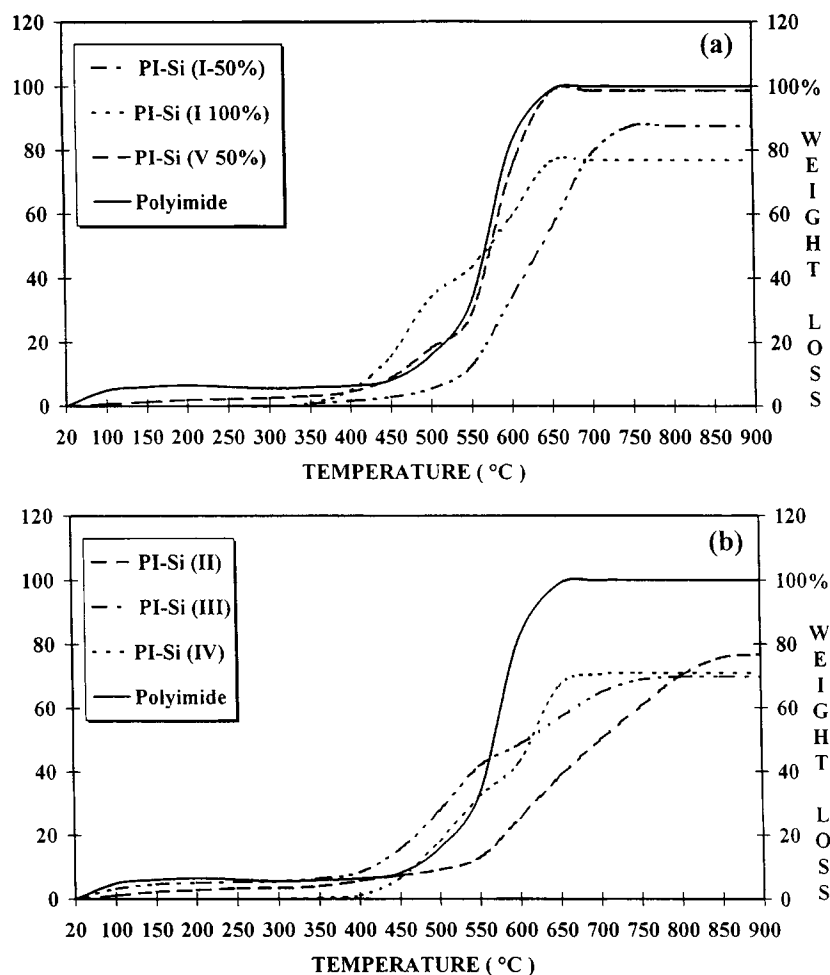and **IV**]. These weight losses are mainly due to the

Figure 11   Thermogravimetric curves obtained on various polyimide–siloxane materials (PI — Si). (a) Polyimide–siloxane linear chains materials, (b) polyimide–siloxane network materials with precursors **II**, **III**, and **IV**.

removal of residual traces of solvents and water. This result clearly indicates that hydrophobic methyl groups (Si — CH$_3$) present in **I** and **IV** facilitate the escape of water during the heat treatment in the polyimide synthesis and give hydrophobic properties to the material. These results confirm the observations already made in the IR study.

SEMs

SEM has been used to study the feasibility and quality of coatings obtained with these materials. All samples present an homogeneous dense coating. The cross sections of the polyimide–silica hybrid materials prepared with precursors **I** and **IV** are

Table III   Experimental and Theoretical Silica Content Obtained on the Various Polyimide–Silicon Materials I, II, III, IV, and V

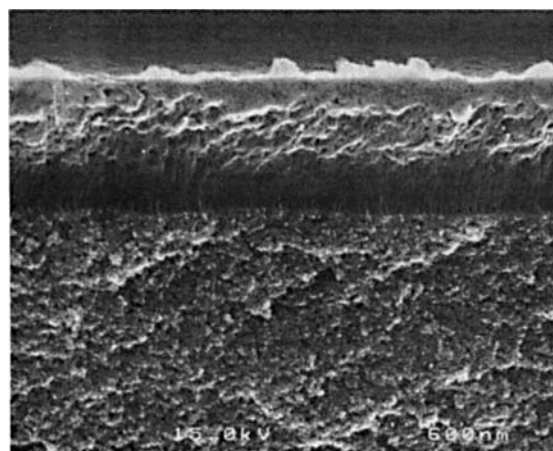|	Material Precursor					
	I 100%	**I 50%**	**II**	**III**	**IV**	**V 50%**
Final weight residue (%)	23.2	12.4	23.2	30.0	29.0	1.3
Theoretical silica content (wt %)	24	13.6	27.5	29.8	28.8	15

presented in Figure 12. The thickness of the hybrid material is about 0.5 μm and 1.5 μm for polyimide–siloxane **I** and **IV**, respectively. This shows the feasability of a homogeneous thin coating with hybrid polyimide–siloxane materials.

CONCLUSION

Polyimide–silica hybrid materials have been successfully prepared by polycondensation, polyimidization, and sol–gel coreactions. Various bonding agents have been used to provide a chemical bonding between the inorganic and the organic phase. DAPTMDS synthesized and DAPrTMDS give linear chain materials, while APrTMOS, APTMOS, and APrMDEOS give reticulated materials. These various materials have been studied by ^{29}Si-NMR and IR spectrometry to compare their molecular structure. ^{29}Si-NMR results show that the synthesis using DAPrTMDS does not succeed in the obtainment of a hybrid material. No silicon is observed in the final material. However, the preparation of hybrid materials using the DAPTMDS is successful. Materials prepared with APrTMOS and APTMOS have been closely compared during their hydrolysis and condensation reactions. This comparison showed that the APrTMOS provides more connected network than APTMOS.

As the different precursors used present more or less hydrophobic or hydrophilic sidegroups, IR study shows that these properties are kept in the resulting materials. TGA confirm these observations and clearly indicates that hydrophobic methyl groups (Si—CH$_3$) present in **I** and **IV** give hydrophobic properties to the material. TGA has been also performed to study the decomposition behavior of all these materials compared to a pure polyimide polymer. TGA indicates that the rate of decomposition of these hybrid polyimides is reduced compared to pure polyimide. This behavior is attributed to the presence of siloxane bonds in the polymer. Finally, the coating feasibility of these various hybrid materials has been tested and observed by SEM. All samples present homogenous and dense coatings. As the coatings obtained with these materials are of good quality; this enables the fabrication of membranes. Perspective work involves dynamic characterizations (gas permeability and selectivity measurements) of these materials and their structure–properties relationships.

(a) 0.6µm
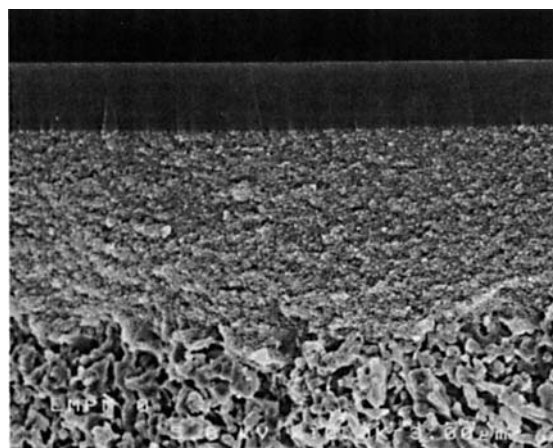
(b) 3µm

Figure 12 SEM micrographs of polyimide siloxane material (PI—Si) cross sections obtained with precursors **I** (a) and **IV** (b).

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