

Organic–Inorganic Polymer Hybrids and Porous Materials Obtained on Their Basis

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ABSTRACT: Tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS), an organic monomer [methylmethacrylate (MMA) or styrene (St)] and either α -propylmethacryloxy- ω -trimethylsiloxy-oligo(dimethylsiloxane) (OMS), as a compatibilizing agent, or α,ω -bis(vinyl) oligo(dimethylsiloxane) (OVS), as compatibilizing and crosslinking agent, were allowed to undergo a sol–gel reaction under acidic condition and in the presence of 2,2'-azoisobutyronitrile (AIBN) as a free-radical initiator. The hydrolysis-condensation and *in situ* free-radical polymerization occur independently, to give a hybrid consisting of both inorganic and organic components. The conversion of the monomers to the proper poly-

mers was monitored by IR spectroscopy and TGA. The resistance of the organic polymers to solvent extraction was also studied. The hybrids were pyrolyzed in an oxidative atmosphere. By decomposition, the organic polymer generated pores in the inorganic matrix. A quantitative evaluation of the characteristics for the resulting porous material was made by determination of the specific area, pore volume, and average radius. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2060–2067, 2003

Key words: organic–inorganic hybrid; sol–gel technique; compatibilization; crosslinking; silicas

INTRODUCTION

Organic–inorganic materials are considered as advanced, innovative materials constituting a very interesting research field. A typical hybrid material contains a crosslinked inorganic phase bound, often covalently, with an organic phase. The properties of the hybrid material can be controlled by the relative amounts of the components.¹ In general, inorganic and organic polymers are immiscible, their incompatibility resulting in biphasic morphology, which has a negative influence on the properties of the obtained material.^{2,3} On the other hand, the biphasic morphology of the hybrid materials can be a starting point to synthesize porous materials. Thus, some materials having the desired porosities can be obtained by using hybrid precursors with certain sizes of phase domains.

The inorganic porous materials constitute a very attractive research field because of their interesting applications in separation techniques,^{4–8} for example, as support for ionic transport liquid membranes,⁹ as catalyst supports, chemical sensing, nanotechnologies, optoelectronic technologies, and supramolecular assemblies.^{6,9–13,14–16} Therefore, there has been great interest in synthesis strategies by which the pore shapes and sizes can be controlled. The basic principle of any strategy is templating, or imprinting, which involves

the formation of the intermediary inorganic–organic assembly. A target molecule, in general low molecular, depending on the material destination, serves as a template for the created assembly. Subsequent removal of the template by solvent extraction, thermal or chemical cleavage, leaves in the inorganic matrix cavities that are complementary to the template in terms of size, shape, and arrangement of functional groups.^{7,10,17,18}

The methods for the preparation of the hybrid systems as precursors are varied.¹⁷ However, most organic/inorganic hybrid composites can be prepared by the sol–gel technique, which allows the preparation of a nanostructured hybrid organic–inorganic materials under mild conditions.^{19–22} The use of oligomers or polymers as templates in the synthesis of porous silica led to the development of convenient synthesis pathways for materials with tailored structures and desirable forms.²³ Different types of oligomers or polymers have already been employed in this kind of synthesis.^{24,25} More recently, organic–inorganic hybrids have been prepared using interpenetrating polymer network (IPN) chemistry. By introducing a polymerizable organic monomer in a sol–gel system, two independent reactions can occur, leading concomitantly to organic and inorganic phases.²⁶ Such a procedure was used in this study: an organic polymer (polymethylmethacrylate or polystyrene), which is formed by *in situ* polymerization in a sol–gel system, according to a previously published procedure,²⁰ was used as a template.

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This study makes an original contribution in that it uses siloxane oligomers end-functionalized with acryl or vinyl groups to decrease the incompatibility between the two phases, such compounds of which are known for their action as surfactants in many bicomponent systems.² Because of their capacities for free-radical polymerization, the organic end groups are incorporated into organic chains. When a bifunctionalized siloxane oligomer is used, this simultaneously causes organic polymer crosslinking. Thus, the network stability will be increased.³ The organic-inorganic hybrids obtained by the above-mentioned strategy were pyrolyzed in air to obtain porous silica as potential selective adsorbents in the separation technique.

EXPERIMENTAL

Materials

Tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), purchased from Merck-Schuchardt (Darmstadt, Germany) were used as received.

The initiator, 2,2'-azoisobutyronitrile (AIBN; Fluka Chemie, Buchs, Switzerland) was purified by recrystallization from abs. methanol.

The α -propylmethacryloxy- ω -trimethylsiloxy-oligo(dimethylsiloxane) (OMS) and α,ω -bis(vinyl) oligo(dimethylsiloxane) (OVS) were obtained by equilibration reaction of the octamethylcyclotetrasiloxane (D₄) with the properly functionalized disiloxane in heterogeneous catalysis according to previously published procedures.²⁷

Commercially supplied methylmethacrylate (MMA) and styrene (St) were freshly distilled in vacuum before use.

HCl 0.1 and 0.5M solutions were used as catalyst.

Procedure

Obtaining organic-inorganic hybrid materials

In a two-neck flat-bottom flask having inert gas inlet and reflux condenser with CaCl₂ protection and magnetic stirrer, the preestablished amounts of tetraalkoxysilane (TMOS or TEOS), organic monomer, end-functionalized siloxane oligomer, and AIBN were charged. An amount of acetone as solvent (for 50% concentration) and 8.76 $\times 10^{-2}$ wt % (with respect to the tetraalkoxysilane amount) HCl as 0.1 or 0.5M solution in water were added. Acetone was chosen as a solvent because it ensures the solvation of all reactants, permits activity at the critic temperature of the free-radical initiator, and can be easily removed from the reaction product. To maintain good homogeneity of the reaction mixture until an advanced stage of the reaction was reached, water was used in only a slight amount as dilution water of the polycondensation

catalyst (HCl). The reaction mixture was stirred at room temperature for 5 h and, subsequently, for 27–110 h (depending on the reactivity of the organic monomer) at 60–65°C under nitrogen, in darkness. The sol usually started to gel after 3–4 days. At the end of the reaction, the volatile fractions (solvent and unreacted monomers) were removed by vacuum distillation and the obtained white to yellowish glassy material was weighed and subjected to extraction in a Soxhlet extractor using chloroform as a solvent. The remaining product was dried in vacuum and weighed to determine the losses by extraction. The spectral and thermal characterizations of the hybrids, before and after extraction, were performed.

After extraction the hybrid materials, compared to the starting material, became more brittle and opaque. This change in the physical aspect was even more evident in the absence of a crosslinker in the reaction mixture.

Conversion of hybrid materials to porous materials

The hybrid material was weighed in a platinum capsule and placed in an oven at 900°C, where the organic polymer was removed by thermal decomposition. The sample was kept in this condition up to a constant weight. Irregular, opaque particles with sizes in the range 0.1–2 mm were obtained after the thermal decomposition step.

Measurements

IR spectra were recorded on a Specord M80 spectrophotometer (Carl Zeiss, Jena, Germany) in the range 200–4000 cm⁻¹. Thermogravimetric analysis data were obtained on a Paulik Derivatograph (Budapest, Hungary) in air at a heating rate of 12°C/min. Non-uniform particles with sizes in the range 0.1–2.0 mm were used for the porosity characterization.

The apparent density (ρ_{ap}) was determined using a mercury pycnometer at 1.333×10^{-4} . The specific density (ρ_{sp}) was measured in *n*-heptane. The surface area was determined by the nitrogen adsorption at the boiling temperature of liquid nitrogen, by the Haul-Dümbgen method on a Ströhlein area meter apparatus (Germany).^{28,29} The mean pore radius was calculated using the following equation, with pores of cylindrical shape assumed:

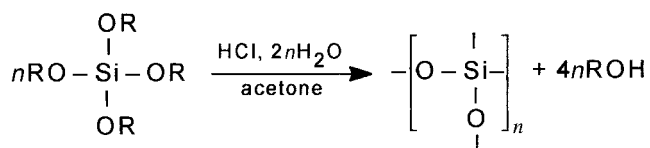
$$r_p = (2V_p/S_{BET}) \times 10^4 (\text{\AA}) \quad (1)$$

where $V_p = (1/\rho_{ap}) - (1/\rho_{sp})$ is the pore total volume (cm³/g).

RESULTS AND DISCUSSION

Obtaining organic-inorganic hybrid materials

A series of organic-inorganic hybrid materials was obtained using a combined technique consisting of a



Scheme 1 General scheme for tetraalkoxysilane hydrolysis and subsequent condensation.

sol-gel standard reaction and an *in situ* radical polymerization. The sol-gel technique permits activity in mild temperature conditions and allows incorporation of different organic molecules having low thermal stabilities by *in situ* polymerization.

Tetraalkoxysilanes (TAOS) as TMOS and TEOS were used as precursors to obtain the hybrid materials by the sol-gel method. They are soluble in common organic solvents, such as acetone, and thus allow effective reactions with various organic compounds. It is known that $\text{Si}(\text{OR})_4$ and its homologs can be rapidly hydrolyzed in the presence of an acid or a base as catalyst. Then, the tetrasilanol undergoes polycondensation reactions, resulting in SiO_2 networks according to **Scheme 1**.

The reaction mechanism of the sol-gel process involving hydrolysis and condensation of tetraalkoxysilane depends on many factors such as catalyst type, water content, and solvent. The catalyst type primarily determines the course of the polycondensation reaction and the final structure of the inorganic matrix.³⁰

In this investigation hydrochloric acid was used as a catalyst because, according to the literature, initial hydrolysis and condensation are rapid and subsequent condensations are very slow in an acid medium. The result of the acid catalysis is a more crosslinked structure. On the other hand, in the base-catalyzed sol-gel reaction of the TAOS, the initial hydrolysis is slow, but subsequent hydrolysis and condensation are rapid, resulting in a highly branched and unreacted monomer.^{31,32} To create the organic phase, monomers such as MMA and St were used, which radical-polymerize in the presence of AIBN.

Another important parameter in the control of hybrid material formation is the crosslinking agent. Its type and quantity have a great influence on the stability of the hybrid network. Ethyleneglycol dimethacrylate is the most frequently used crosslinking agent. An alternative is divinylbenzene, although this is used less in such systems.³³ In this study, the end-functionalized siloxane oligomers with organic groups (propylmethacryloxy or vinyl), which are able to radical-polymerize, were used to ensure good compatibilization between the organic and inorganic components and/or crosslinking of the organic phase to increase the stability of the network. It is presumed that the organic groups on the ends of the siloxane oligomers will diminish the incompatibility between the two

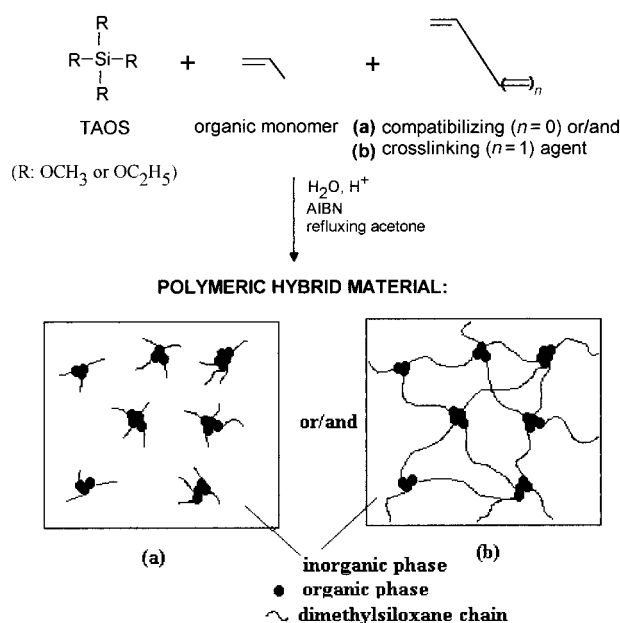
phases by reducing the surface tension or increasing the adherence between phases, thus permitting the formation of some more stable polymeric dispersions.² In addition, by using the telechelic functionalized siloxane oligomers, a crosslinking of the organic polymer occurs. The free-radical copolymerization of the styrene and its derivatives with α,ω -unsaturated siloxane polymers was previously reported.^{3,34,35}

The organic-inorganic hybrid materials obtained in this study, according to a conventional classification,^{12,33} belong to class II, which corresponds to the hybrid materials containing both weak and strong covalent bonds between the two component types. The general strategy used in this work for the synthesis of the organic-silica hybrid materials is presented in **Scheme 2**.

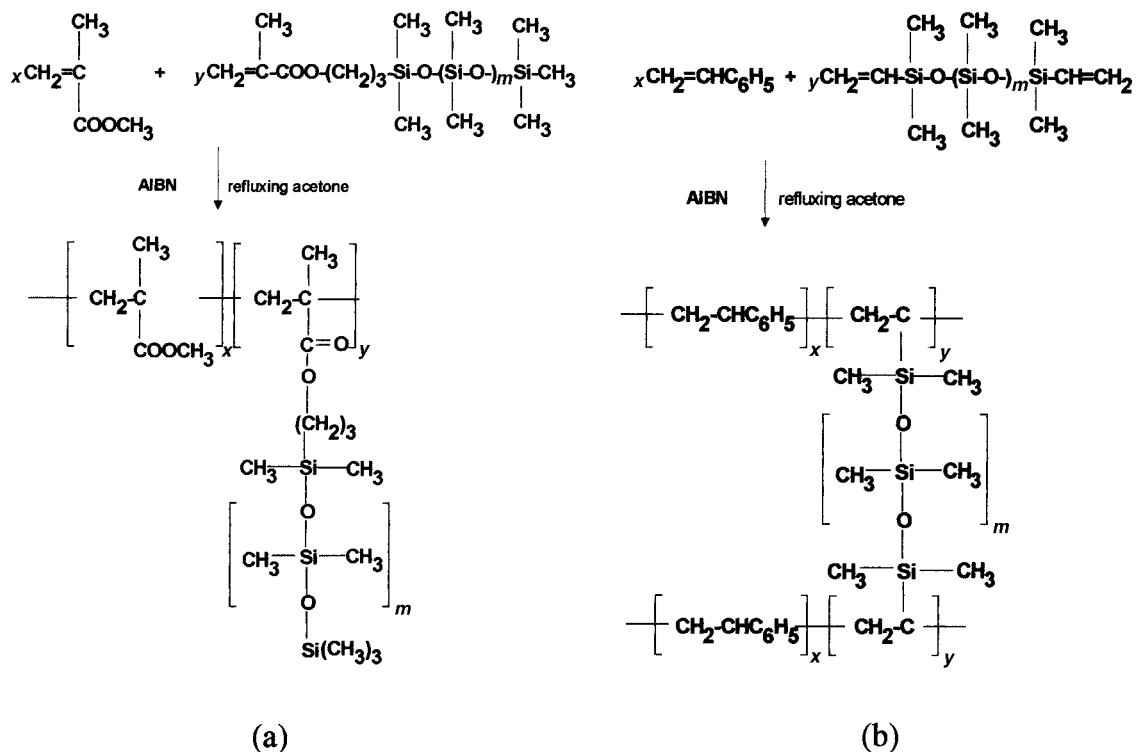
The incorporation of the mono- or bifunctionalized siloxane oligomers in the organic network is presented in **Scheme 3**.

The influence of various factors (organic monomer, alkoxy silane, compatibilizing or crosslinking agent, catalyst concentration) on the characteristics of the hybrid precursors and porous silica obtained on their basis was studied. The experimental conditions for the synthesis of hybrid materials are presented in Table I.

The IR spectra of the hybrid materials show all expected characteristic peaks: 1200–1000 cm^{-1} (asymmetrical stretch for $-\text{O}-\text{Si}-\text{O}-$), 2950, 1430, 1280, and 800 cm^{-1} (for methyl groups). A broad band appears at 3700–3200 cm^{-1} . The characteristic absorption band of silanol groups ($\text{Si}-\text{OH}$) formed during the hydrolysis of the alkoxy groups in TMOS or TEOS (Fig. 1, curves marked as a) could be enclosed in this band



Scheme 2 Illustrative route for the synthesis of hybrid materials.



Scheme 3 Incorporation of the siloxane oligomer in the organic network: a-as compatibilizing agent; b-as compatibilizing and crosslinking agent.

beside other OH groups. Given that the other characteristic band for Si—OH groups at 950 cm^{-1} frequently appeared as a shoulder, we presume that the polycondensation reaction occurred to a very high degree. The characteristic peaks of the organic polymers are also present in the IR spectra of the hybrid materials: the C—H stretching vibration band at 2950 cm^{-1} for any organic component or the carbonyl stretching band in PMMA at 1745 cm^{-1} . The specific absorptions for the initial double bond from organic monomer and end groups of the siloxane oligomers (1600 cm^{-1}) also disappear from IR spectra as a result of their polymerization.

The TGA curves of hybrid materials in air are shown in Figure 2. The weight loss below 100°C corresponds to the residual solvent. The onset of polymer decomposition is around $320\text{--}350^\circ\text{C}$. A fast and continuous weight loss is observed in the $320\text{--}520^\circ\text{C}$ region. Silica constitutes the final residue, confirmed by IR spectra [Fig. 1(c)]. The thermooxidative stability of the hybrid material depended on the content of the organic component: the lower the content of the organic component, the higher the thermal stability, as expected.

The composition of the hybrid materials before and after extraction could be calculated on the basis of the

TABLE I
Experimental Conditions for Synthesis of Organic-Silica Hybrid Materials^a

Sample	Tetraalkoxy silane (TAOS)	Organic monomer (OM)	Compatibilizing/crosslinking agent (CA)	Feed molar ratio (TAOS/OM/CA)	HCl solution conc. (M)	Reaction time: room temp./reflux (h)	Yield (%)
1	TMOS	MMA	OVS	1/1.5/1	0.5	5/98	90
2	TMOS	MMA	—	1/1.5/0	0.5	5/110	93.5
3	TMOS	MMA	OVS	1/1.5/1	0.1	5/110	95.1
4	TEOS	MMA	—	1/1.5/0	0.5	5/62	98.5
5	TEOS	MMA	OVS	1/1.5/1	0.5	5/85	97.2
6	TMOS	St	OVS	1/1.5/1	0.5	5/33	62.5
7	TMOS	St	—	1/1.5/0	0.5	5/46	59.7
8	TMOS	St	OVS	1/1.5/1	0.1	5/27	60.4
9	TEOS	St	OVS	1/1.5/1	0.1	5/57	82.2

^a 2 wt % AIBN, 8.76×10^{-2} wt % HCl as aqueous solution 0.5 or 0.1M, in refluxing acetone.

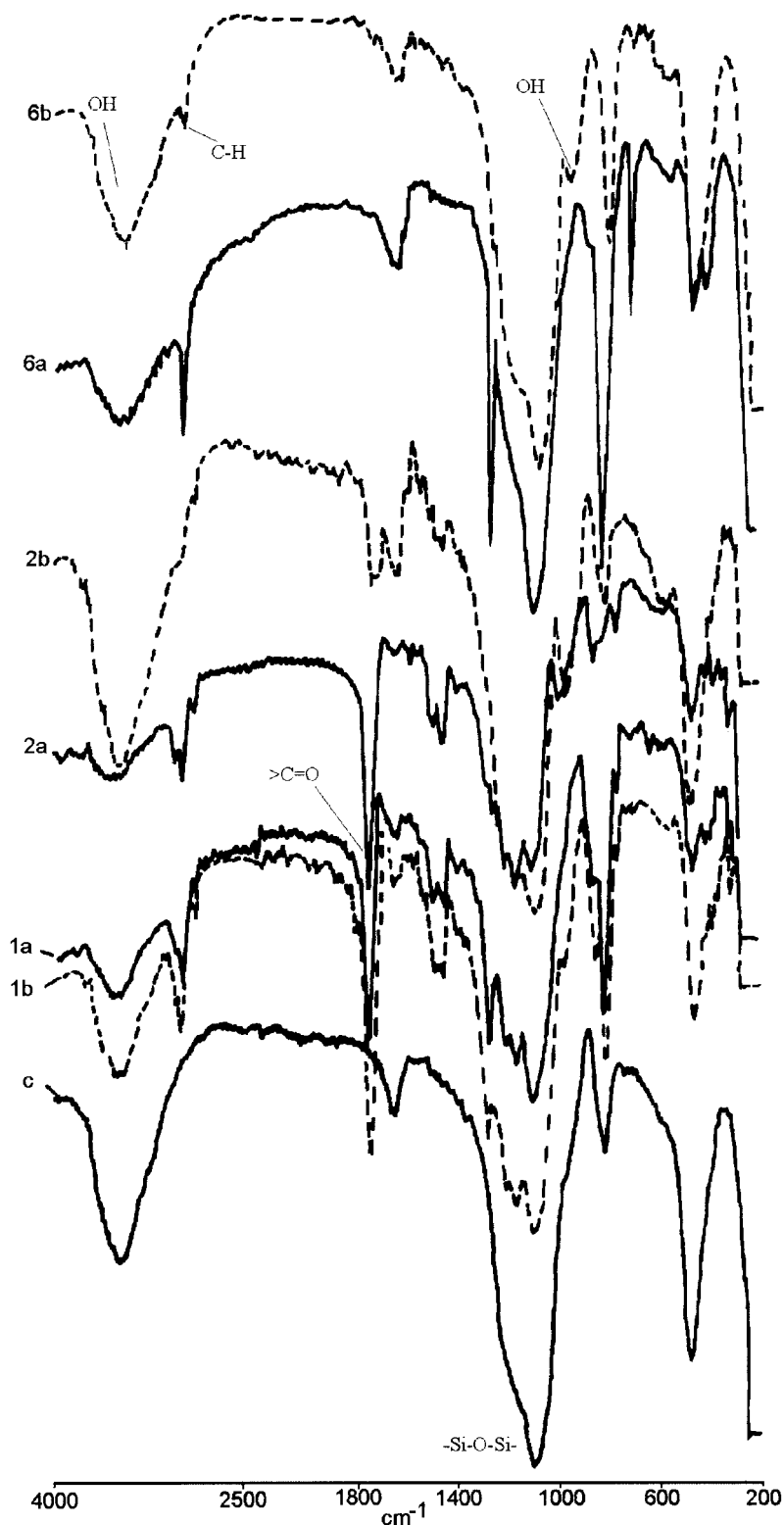


Figure 1 IR spectra of some hybrid materials (1: TMOS : MMA : OMS = 1 : 1.5 : 1, HCl sol. 0.5M; 2: TMOS : MMA = 1 : 1.5, HCl sol. 0.5M; 6: TMOS : St : OVS = 1 : 1.5 : 1, HCl sol. 0.5M] in various stages: (a) before extraction; (b) after extraction; (c) after calcination.

remaining residue at 900°C, and the obtained results are included in Table II.

The hybrid network stability to solvents was evaluated by gravimetric measurements or thermo-

gravimetric analysis before and after extraction in a Soxhlet extractor using chloroform as a solvent. The mass losses ($L\%$) were calculated on the basis of the organic component content before (O_i) and after

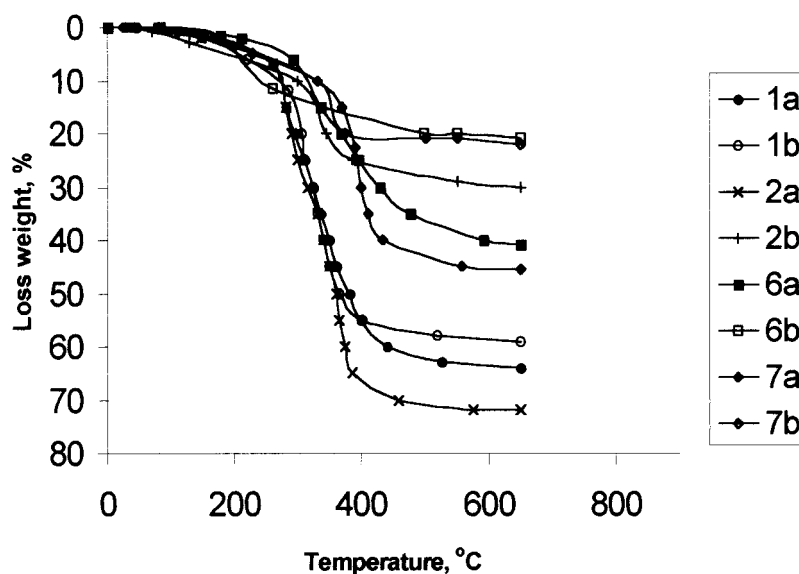


Figure 2 TGA traces for the silica-organic hybrid materials (1: TMOS : MMA : OMS = 1 : 1.5 : 1, HCl sol. 0.5M; 2: TMOS : MMA = 1 : 1.5, HCl sol. 0.5M; 6: TMOS : St : OVS = 1 : 1.5 : 1, HCl sol. 0.5M; 7: TMOS : St = 1 : 1.5, HCl sol. 0.5M): (a) before extraction; (b) after extraction with solvent.

extraction (O_f), respectively, using the following relationship:

$$L\% = 100(O_i - O_f)/O_i \quad (2)$$

As one can see from Table II, significant differences are evident between the extraction losses of the hybrids, depending on the starting components. The extraction losses were lower with about 40–50 wt % for the hybrids obtained by using a crosslinking agent compared to those ones obtained without this. A qualitative evaluation by IR spectrophotometry also was made. The relative intensity of the characteristic peak for the organic component (C—H band at 2950 cm^{-1}) was reduced after extraction, compared to that of the —Si—O—Si— band at $1000\text{--}1200\text{ cm}^{-1}$ (Fig. 1, the curves marked as b). This decrease is more pro-

nounced in the absence of the crosslinker [Fig. 1, 2(b)]. Another observation is that the network stability to solvent appears to be higher when a lower quantity of water was introduced in the initial reaction mixture (0.5M HCl solution compared with 0.1M HCl solution): for example, Sample 1 compared with 3, and 6 with 8, respectively. Also, the hybrids based on MMA (Samples 1 and 2) appear to be more stable than those derived from St (Samples 6 and 7).

Conversion of hybrid materials to porous materials

This process was made by pyrolysis at 900°C in an oxidative atmosphere to a constant weight, when the template (organic polymer) was removed. The complete decomposition was verified by IR spectro-

TABLE II
Some Characteristics of the Obtained Hybrids: Solvent Resistance and Thermooxidative Stability

Sample ^a	Organic component before extraction, O_i (wt %) ^b	Losses by extraction, L (wt %) ^b	Organic component after extraction, O_f (wt %) ^b	Porous material remaining after pyrolysis (wt %) ^c
1	63	7.9	58.0	42.4
2	72	59.3	29.3	70.9
3	64	12.3	56.1	43.9
4	59	52.5	28.0	71.2
5	51	11.8	44.9	54.8
6	41	48.7	21.0	79.2
7	47	59.5	19.0	81.9
8	46	58.7	18.9	80.3
9	35	16.6	29.2	70.9

^a As in Table I.

^b Determined on the basis of TGA curves traced out before and after extraction of the samples with solvent.

^c Determined gravimetrically and reported with respect to the material amount before calcination.

TABLE III
Overall Morphological Characteristics for the Porous Silica Obtained in Various Conditions

Sample ^a	V_p (cm ³ /g)	S_{sp} (m ² /g)	r_p (Å)
1	0.4657	524	17.8
2	0.2263	242	18.7
3	0.3667	579	12.7
4	0.2566	92	55.9
5	0.2078	471	8.8
6	0.2072	335	12.4
7	0.3643	—	—
8	0.3474	490	14.2
9	0.2339	327	14.3

^a As in Table I.

tometry that compared the spectrum of the pyrolyzed material with that characteristic for a pure silica material. The yields in the porous materials are also presented in Table II. The yield data are in good agreement, almost complementary, with the determined organic content of the extracted hybrid materials. The small differences arise from the solvent traces retained in the hybrid material after extraction.

Morphological characterization of the obtained porous silica was made by the surface area, pore volumes, and average radius. The obtained values are presented in Table III. As one can see from Table III, all samples have pore radii in the range 0.883–1.778 nm.

By comparing the data from Table III one may observe that, by using end-functionalized siloxane oligomers as compatibilizing or/and crosslinking agents in the synthesis of the hybrid materials (Samples 1, 3, 5, 6, 8, and 9), higher values for specific areas (327–579 m²/g) were obtained than those in the case when these components were absent (Samples 4 and 2, 92 and 242 m²/g, respectively). Also, by using HCl in a more diluted solution, which involves the introduction of a higher water quantity in the system, the specific area of the obtained porous material is increased (Table III, Sample 1 compared with 3, and sample 6 compared with 8).

The specific area was lower when TEOS was used as a precursor (Sample 1 compared with 5, 2 with 4, and 8 with 9, respectively). Also, the specific area values were much higher when MMA was used as a template than in the case of St. We presume that the similarity between the end group of the compatibilizing agent (OMS) and the MMA permits a better mixing of the organic and inorganic phases.

CONCLUSIONS

A combined technique consisting of the sol–gel reaction of alkoxy silanes and *in situ* radical polymerization of some organic monomers was applied in the synthesis of some organic–inorganic hybrids. A

mono- or bi-end-functionalized siloxane oligomer was used for the first time as a compatibilizing and/or a crosslinking agent to improve both the miscibility of the components and the network stability to solvents. The studies on thermooxidative stability and solvent resistance of the obtained hybrids revealed that the hybrids having a lower content of the organic component were more thermally stable. The stability to solvent increased by using a compatibilizing/crosslinking agent, in the presence of more concentrated HCl solution and when MMA was used as an organic monomer.

These hybrids were pyrolyzed in air and porous silica, having a specific area between 92 and 579 m²/g and pore radius in the range 0.883–1.778 nm, was obtained. The increase in specific area and the decrease in pore radius were emphasized by using the end-functionalized siloxane oligomers. The other parameters, such as water quantity and alkoxy silane or organic monomer type used for obtaining hybrid material, also influenced the overall characteristics of the resulting porous silica. The specific area increased when MMA was used as a template, and TMOS was used as a precursor for the inorganic matrix. For pore radius an almost identical trend was observed. Based on the characteristics of the obtained porous silica, we postulate that these materials can be suitably selective adsorbents in the separation technique. Further investigations on this aspect are in progress now.

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