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Preparation of 2,5-diphenyloxazole doped sol-gel glasses and their application to radio-analytical chemistry

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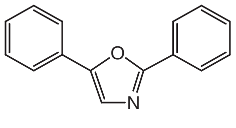
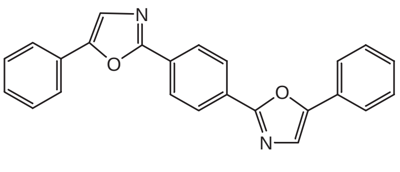
Transparent, colourless, monolithic sol-gel glasses doped with 2,5-diphenyloxazole (PPO) at different concentrations were prepared *via* the polymerisation of tetraethyl orthosilicate (TEOS) in a H_2O–AcOH–EtOH–PPO solution. The gel samples were aged at room temperature, and dried in two stages: first at room temperature, then at 70 °C to reduce possible fracture. They have pore diameters in the range 1.8–2.1 nm. The leaching of PPO from the sol-gel glass was monitored using ultraviolet (UV) and X-ray photoelectron spectroscopy (XPS). The results show that the sol-gel glasses dried at the higher temperature leach less than those dried at room temperature. These sol-gel glasses, either in monolith or powder form, are effective in detecting β^- radioactivity.

Introduction

The development of liquid scintillation counting in the early 1960s has had a dramatic effect on the use of radioisotopes, particularly in the physical and life sciences.[1,2] The main reason for this is that the two most widely used radioisotopes in this area, ^3H and ^{14}C, are both weak β^- emitters, so that other counting techniques such as ionisation, Geiger–Müller and proportional counting are either impractical or have serious limitations. The advantages of liquid scintillation counting for weak β^- emitters are many: (a) high efficiency, typically $>50\%$ for ^3H and $>90\%$ for ^{14}C; (b) high sample throughput as instrumentation is easily automated; and (c) a wide range of samples, from simple organic to complex biological, can be analysed.[3,4]

The need for further improvement stems from the general tightening in radioactive waste legislation that has been in evidence over the last decade.[5] A liquid scintillator consists of a solvent, a primary solute (*e.g.* 2,5-diphenyloxazole) and, sometimes, a secondary solute {*e.g.* 1,4-di[2-(5-phenyloxazolyl)benzene], POPOP}. The radioactive sample is either dissolved directly in the scintillator, or if insoluble, through the addition of a blending agent or secondary solvent—dioxane is frequently used for this purpose. Cocktails have been developed so as to maximise the amount of aqueous samples that can be dissolved in the scintillator.[3,4] After counting it is customary practice to dispose of the radioactivity *via* the drains or absorb it onto vermiculite. Large numbers of samples can generate a considerable volume of waste. Ideally the radioactive waste should be stored in as compact a form as possible and the work necessary to bring it to this state should be kept to a minimum. Hence, a counting method requiring minimum use of solvent and recycling of the primary/secondary solute would represent a major advance in radio-analytical chemistry technology.


PPO


POPOP

The sol-gel method is a convenient low temperature route to converting metal alkoxides into the corresponding inorganic gels and glasses under relative mild conditions.[6] An appropriate precursor, such as tetraethyl orthosilicate (TEOS) undergoes acid catalysed hydrolysis [eqn. (1)], followed by condensation polymerisation [eqn. (2)] at low temperature in a suitable solvent to form the polymeric silica network.

$$Si(OEt)_4 + 4H_2O \rightarrow Si(OH)_4 + 4\ EtOH \qquad (1)$$

$$n\ Si(OH)_4 \rightarrow n\ SiO_2 + 2n\ H_2O \qquad (2)$$

The low temperature provides a clean route for doping inorganic gels and glasses with organic molecules, and in the process makes it possible to develop composite materials with specific properties, and hence opens the way to various potential applications. For example, organic doped sol-gel glasses, ranging from monoliths to thin films, have been developed as sensors for metal cations,[7–10] protons (H^+),[9–13] anions,[14,15] neutral species,[16–19] oxygen[20] or carbon monoxide[14] in water, and oxygen[21] or carbon monoxide[21,22] in the gas phase.

We sought to incorporate PPO into a sol-gel silica monolith in order to exploit fully its eventual sensing properties in radio-analytical chemistry technology. The chemical and physical properties of the PPO are hopefully retained, whilst the pore network allows external molecules, tritiated water (HTO) in this case, to diffuse into the matrix and interact with the solute. In this paper we report a preliminary investigation into the preparation and characterisation of sol-gel glasses doped with PPO at different concentrations. Pore size, surface area and leaching tests and application in detecting ^3H radioactivity are of particular interest.

Experimental

Materials

TEOS (Aldrich, 98%), TMOS (Acros, 99%), glacial acetic acid (Fisons, Anal.), absolute alcohol 100 (Hayman Ltd., 99.86%), PPO (Acros, scintillation grade), toluene (Fisons, low in sulfur, Anal.) were used as received.

Instrumentation

BET surface areas and pore sizes were measured on a Coulter SA3100 Surface Area and Pore Size Analyser. The samples were outgassed at 120 °C for 240 min. UV spectra were recorded using a Philips PU8740 UV/VIS Scanning Spectrophotometer. Liquid scintillation counting was carried out using a Packard Tri-Carb 1500 Liquid Scintillation Analyser, toluene was the preferred solvent. XPS measurements were made using a VG Scientific ESCALAB Mk II Spectrometer interfaced with a VG500S data system based on a DECPDP 11/73 computer. The operating conditions were as follows: the X-ray source (Mg-Kα 1253.6 eV radiation) was operated at a power of 450 W (*i.e.* 13 kV potential and 34 mA emission current). The spectrometer was operated in the fixed analyser transmission mode at a pass energy of 50 eV. The base pressure in the sample chamber during analysis was approximately 3×10^{-8} mbar. The sample was kept in the preparation chamber under vacuum overnight.

Preparation of PPO doped sol-gel monolith

Typically a mixture of TEOS (10.2 cm^3, 45.8 mmol), water (1.65 cm^3, 91.5 mmol), ethanol (8.1 cm^3, 137.3 mmol), acetic acid (0.2 cm^3) and PPO (amount appropriate for concentration required) was obtained as a clear, colourless solution. A portion of the solution (2.0 cm^3) was sealed in a glass vial (20 cm^3). Usually 10 such vials were prepared for one particular PPO concentration at a time. These vials were then kept at room temperature to gel (1 week) and age (1 week) under normal atmosphere. The gels were then allowed to dry at room temperature for one week, followed by drying at 70 °C overnight. Sol-gel glasses were obtained as clear, colourless and fracture-free monoliths in cylindrical disc form.

Leaching test

Leaching tests were carried out using UV and XPS methods. For UV monitoring, sol-gel glass was ground to a powder form. To an UV cell (quartz, 1 cm) filled with toluene (3 cm^3), was added a known amount of sol-gel glass sample. The mixture was shaken at regular intervals to be mixed thoroughly. UV spectra were recorded at various time intervals to obtain the profiles of PPO concentration in the solution, while the solids separated from the solution and settled at the bottom of the cell. For XPS analysis, four sol-gel glass discs, representing PPO concentrations at 0, 1, 2 and 4 g dm^{-3}, were used without further treatment. Another four sol-gel glass discs were packed in a small column, separated by filter papers and thoroughly washed by a constant toluene stream that was maintained at a rate of 2 cm^3 min^{-1}. The sol-gel glasses were then dried at 70 °C overnight and then mounted on the XPS sample stand using 'super glue' for analysis.

Liquid scintillation counting procedure

To a micro-vial (0.5 cm^3) was added stock HTO solution in 1,4-dioxane, toluene (0.4 cm^3) and sol-gel glass powder (0.05–0.2 g). The micro-vial was then inserted into a standard glass scintillation vial (25 cm^3), and counted for 5 min for good statistical disintegration per minute (DPM) values.

Results and discussion

Sol-gel preparation

Both TMOS and TEOS were used in trials to prepare PPO doped sol-gel glasses. At room temperature, gelation for both HCl catalysed systems was slow. Acetic acid catalysed systems gave fracture-free gels. Without catalyst, precipitation of white solids was observed in the TEOS system. We therefore decided to use the system containing TEOS–EtOH–H$_2$O–AcOH (see Table 1). To avoid fracture, the gels were aged at room temperature for a week, whilst the vials containing the gel were kept tightly closed to avoid the loss of solvents. After ageing the gels were dried in two stages: first at room temperature with around 5% (w/w) weight loss per day for one week. Fracture-free, transparent and disc-shaped sol-gel glasses were obtained after further drying at 70 °C overnight. The temperature is just slightly below the melting point of PPO (72–74 °C). All operations were carried out under normal atmosphere.

Table 1 Preparation of PPO doped sol-gel glasses[a]

No.[b]	Composition of each vial/mmol: TEOS	EtOH	H$_2$O	AcOH	PPO	Fracture-free gel?	Colourless monolith upon drying?
1	4.58	13.73	9.15	0.35	0.000	Yes	Yes
2	4.58	13.73	9.15	0.35	0.014	Yes	Yes
3	4.58	13.73	9.15	0.35	0.027	Yes	Yes
4	4.58	13.73	9.15	0.35	0.054	Yes	Yes

[a] Duplicates of 10 vials were prepared. The mixture was acidic (pH 3.5). Gelation and aging were carried out at room temperature. The final drying temperature was 70 °C. [b] The same numbering system was used throughout Table 1–5. Each number refers to the monolithic sol-gel glasses which were prepared in the same batch with identical PPO concentration.

Surface area and pore size

Surface area and pore size data are summarised in Table 2. The average pore diameter (d) is estimated from $d=4V/S$, where V is the total pore volume and S is the surface area. The Coulter SA3100 Analyser uses the gas sorption method; the inert gas adsorbate is nitrogen. The BET (Brunauer, Emmett, Teller) calculation is used for the determination of the sample specific surface area. The BJH (Barrett, Joyner, Halenda) calculation yields the pore size distribution. Coulter VacJack sample tubes, which minimise the effects of changing liquid cryogen level as cryogen boils away during long pore parameter analysis, were used. By using these sample tubes BET surface area reproducibility was better than ±2%.[23] These PPO doped sol-gel samples have very similar surface areas. PPO concentration (up to 2×10^{-2} M) did not seem to affect the surface area or average pore diameter.

Leaching

PPO was reported to display a high intensity absorption band in the 300–335 nm region due to the π–π* through conjugate transition in the aromatic structure. Fine details of this absorption band are recognisable in cyclohexane solution, with peaks at 302 and 318 nm, plus shoulders at 310 and 333 nm.[24] In toluene, PPO (9×10^{-3} M) also displays a very similar absorption band with peaks at 307 and 319 nm, plus shoulders at 311 and 335 nm. Hyperchromic effects were observed when toluene was replaced by EtOH or TEOS as solvent. However, as observed in the BET surface analysis experiments, sol-gel glasses dried at 70 °C only lose a further 5% weight when subjected to heat treatment at 120 °C for 4 h. This means that the level of any volatile residue, such as solvent (EtOH), catalyst (AcOH) or unreacted starting materials (water, TEOS) will not exceed 5% in weight. A 100 mg sol-gel glass sample can release *ca.* 5 mg impurity to the 3 cm^3 of toluene in a UV cell. UV absorptions of PPO in toluene spiked with 0.2% (v/v) impurity such as EtOH, AcOH or TEOS were all identical. The cut-off wavelength for toluene is 285 nm[25] and

Table 2 Surface area and pore size measurements

No.	Drying temp./°C	Surface area S/m^2 g^{-1}	Average pore diameter d/Å
1	70	610	21
2	70	540	20
3	70	506	20
4	70	515	21

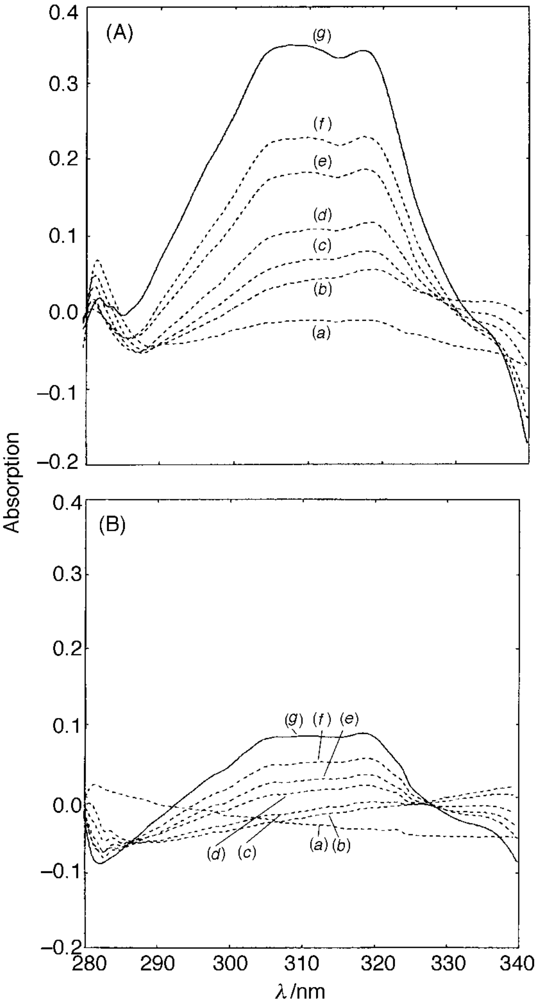


Fig. 1 Changes in UV spectra, representing PPO leaching from (A) sol-gel glass (No. 4 in Table 1) dried at room temperature and (B) sol-gel glass (No. 4 in Table 2) dried at 70 °C. These spectra were recorded at (*a*) 0, (*b*) 2, (*c*) 5, (*d*) 10, (*e*) 20, (*f*) 30 and (*g*) 60 min after mixing the sol-gel glass with toluene in a UV cell.

the main absorption band for PPO is in the 300–335 nm region. With these factors in mind, together with the advantage of monitoring the leaching in toluene which is the major scintillation solvent, the choice of toluene as solvent was entirely satisfactory.

UV spectra representing the PPO concentrations in toluene are shown in Fig. 1. The increase of PPO concentration reflects the leaching from sol-gel glasses in a semi-quantitative manner. The rate of leaching was greater in the earlier stage of the mixing, then decreased gradually for sol-gel glasses dried at room temperature [Fig. 1(A)]. Sol-gel glasses treated at higher temperatures should have shrunk structures, and tend to leach less than their room temperature dried counterparts during the same period [Fig. 1(B)]. XPS analysis (Table 3) of the toluene-treated sol-gel glasses showed that the surface was free of PPO. This observation also supports the UV results that the PPO concentration increased in the toluene solution due to leaching at the sol-gel surface or outer layers. However, PPO was also encapsulated in the inner pores, and sufficient concentration was retained after the toluene treatment. These sol-gel glasses still gave more than 60% relative efficiency when used in liquid scintillation counting (see Table 5).

Table 3 XPS analysis of PPO doped sol-gel glasses before and after treatment in toluene

	Before (atomic %)				After (atomic %)			
No.	C	O	Si	N	C	O	Si	N
1	8.2	72.4	19.0	0.5	7.8	72.8	19.5	0.0
2	10.6	70.3	18.0	1.2	6.5	73.9	19.6	0.0
3	10.3	69.4	18.9	1.4	8.1	71.5	20.5	0.0
4	18.9	63.1	14.8	3.3	8.6	72.7	18.7	0.0

Table 4 Counting efficiency for PPO doped sol-gel glasses in EtOH–toluene mixture

No.	Sol-gel glass/g	HTO sample/g	Radioactivity/ dpm g^{-1}	Relative efficiency (%)^a
1	0.076	0.3616	22904	74.6
2	0.059	0.3602	25318	82.5
3	0.057	0.2608	26863	87.5
4	0.060	0.3545	27367	89.2

[a] Compared to a toluene-based scintillator (3.4 g dm^{-3} PPO). Standard HTO radioactivity = 30694 dpm g^{-1}.

Table 5 Counting efficiency for PPO doped sol-gel glasses after toluene wash in EtOH–toluene mixture

No.	Sol-gel glass/g	HTO sample/g	Radioactivity/ dpm g^{-1}	Relative efficiency (%)^a
1	0.125	0.4116	60409	66.8
2	0.104	0.4130	65965	73.0
3	0.111	0.4139	59698	66.0
4	0.059	0.4115	70140	77.6

[a] Compared to a toluene-based scintillator (3.4 g dm^{-3} PPO). Standard HTO radioactivity = 90408 dpm g^{-1}.

Liquid scintillation counting using PPO doped sol-gel glasses

The efficiency of PPO doped sol-gel glasses to detect β^- radioactivity (from tritiated water, HTO) was investigated using a liquid scintillation counting method. Preliminary results are shown in Table 4 and 5, and the counting efficiency was compared with the standard PPO solution in toluene as scintillator. When sol-gel glasses were used with toluene alone, the relative efficiency was very low, possibly due to some preferential absorption of water molecules onto the glass. It is also possible that hydrogen–tritium (H–T) exchange takes place on the surface Si–OH groups.[26] This can gave rise to chemical quenching because at this stage it appears that the PPO released from the freshly broken surface was the effective fluor. The energy of radiation was not freely passed between the solvent and fluor molecules, thus fewer photons were generated. However, with careful adjustment of the scintillation cocktail, in this case by adding EtOH to suppress the surface H–T exchange or preferential absorption, high efficiency, typically >60%, can still be achieved. The liquid scintillation counting method provides important clues about the effectiveness of sol-gel encapsulation. Furthermore it may yield more information about the mechanistic details as to how radioactivity interacts with the solvent and fluor within/outside the sol-gel cages. Further work designed to improve our understanding is in progress.

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