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Covalent Incorporation of 2,5-Diphenyloxazole in Sol−Gel Matrices and Their Application in Radioanalytical Chemistry

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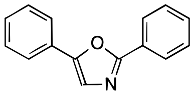
4-Hydroxymethyl-2,5-diphenyloxazole (4-$HOCH_2$-PPO, **3**) was reacted with 3-isocyanatopropyltriethoxysilane (3-ICPS, **4**) to form a functionalized silicon alkoxide precursor (3-ICPS-PPO adduct **5**). Transparent, colorless, monolithic sol−gel glasses with **3** covalently incorporated at different concentrations were prepared via the copolymerization of tetraethyl orthosilicate (TEOS) and **5** in a $H_2O/CH_3COOH/C_2H_5OH$ solution. The gel samples were aged at room temperature, and dried in two stages: first at room temperature, and then at 70 °C, to reduce possible fracture. They have pore diameters in the range 2.2−2.4 nm. By comparison with the simple entrapment procedure, the leaching of scintillator from the sol−gel glass formed as a result of covalent bonding is greatly reduced. Furthermore, these sol−gel glasses are highly efficient at detecting β^- radioactivity.

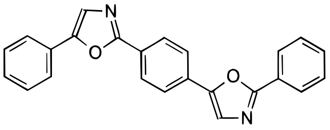
Introduction

Two of the most widely used radioisotopes in the physical and life sciences, ^3H and ^{14}C, are both weak β^- emitters so that counting techniques such as ionization, Geiger−Müller, and proportional counting are either impractical or have serious limitations.[1,2] The advantages of liquid scintillation counting, which was first developed in the early 1960s for counting 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 analyzed.[3,4]

A liquid scintillator consists of a solvent, a primary solute (e.g., 2,5-diphenyloxazole, PPO) and, sometimes, a secondary solute [e.g., 1,4-bis(5-phenyloxazol-2-yl)-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 maximize the amount of aqueous sample that can be dissolved in the scintillator.[3,4] After counting, it is a customary practice to dispense the radioactive materials via the drains or absorb it onto vermiculite. The need for further improvement stems from the general tightening in radioactive waste legislation that has been in evidence over the past decade.[5] 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 radioanalytical chemistry.



PPO



POPOP

The sol−gel method is a versatile low-temperature route to converting metal alkoxides into the corresponding inorganic gels and glasses, under relatively mild conditions.[6−9] An appropriate precursor, such as tetraethyl orthosilicate (TEOS) undergoes hydrolysis (1), followed by condensation polymerization reactions (2 and 3), at low temperature in a suitable solvent to form the polymeric silica network. Equations 1−3 are a simplified representation of the complex reactions which

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can occur:

$$\mathrm{Si(OEt)_4} + n\mathrm{H_2O} \rightarrow \mathrm{Si(OEt)_{4-n}(OH)_n} + n\mathrm{EtOH} \quad (1)$$

$$\equiv\mathrm{Si{-}OEt} + \mathrm{HO{-}Si}\equiv \rightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{EtOH} \quad (2)$$

$$\equiv\mathrm{Si{-}OH} + \mathrm{HO{-}Si}\equiv \rightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{H_2O} \quad (3)$$

The low-temperature process provides a clean route for doping inorganic gels and glasses with organic molecules. This makes it possible to develop composite materials with specific properties, for example sensors.[10,11]

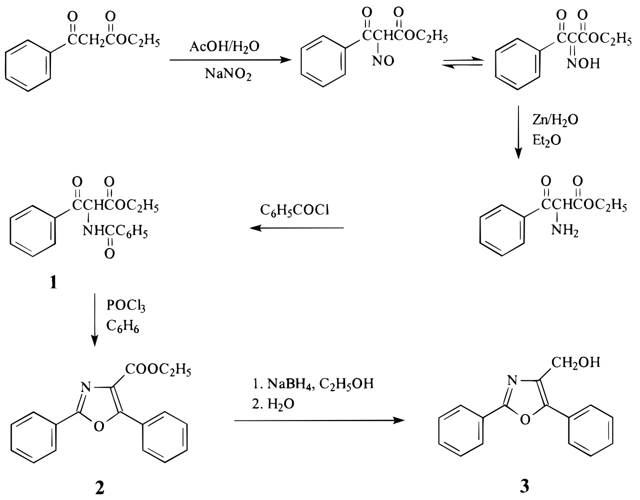
In our previous work,[12] we sought to entrap PPO in a sol−gel silica monolith to exploit its sensing properties in radioanalytical chemistry. The porous network allows external molecules, tritiated water (HTO) in this case, to diffuse into the matrix and interact with the solute. The energy transfer was largely uninterrupted by the presence of the sol−gel matrices. The disadvantage was that the mobility of the PPO molecules within the sol−gel matrix caused migration out of the matrix. Leaching therefore prevents the use of a sol−gel glass of this kind as a sensor material. Covalently bonding the entrapped species to the glass by copolymerization of trialkoxysilane [usually $-\mathrm{Si(OCH_3)_3}$ or $-\mathrm{Si(OCH_2CH_3)_3}$] end-capped dopants, such as organic reagents,[13−16] enzymes,[17] or oligomers or polymers,[18−20] with sol−gel precursor has been shown to be an efficient solution to leaching problems. In this paper we address the leaching problem by covalently bonding the scintillator to the sol−gel matrices through a urethane linkage. Other properties of the covalently incorporated sol−gel glasses, such as pore size, surface area, and counting efficiency in detecting ^{3}H radioactivity are also reported.

Experimental Section

Materials. TEOS (Aldrich, 98%), tetramethyl orthosilicate (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.), 3-isocyanatopropyltriethoxysilane (Avocado, 95%), and triethylamine (Aldrich, 99%) were used as received.

Instrumentation. BET (Brunauer, Emmett, Teller) surface area and pore size measurements were carried out on a Coulter SA3100 surface area and pore size analyzer. UV spectra were recorded using a Philips PU8740 UV/vis scanning spectrophotometer. Liquid scintillation counting was performed on a Packard Tri-Carb 1500 liquid scintillation analyzer, and XPS surface analysis was carried out using a VG Scientific ESCALAB Mk II spectrometer. Detailed experimental procedures were described previously.[12]

Scheme 1



4-Hydroxymethyl-2,5-diphenyloxazole (3). This compound was synthesized from the commercially available ethyl benzoyl acetate following literature precedents (Scheme 1).[21,22] A mixture of ethyl benzoyl acetate (22.2 g, 0.12 mol), acetic acid (45 cm^3), and water (15 cm^3) was cooled to <5 °C in a three-necked flask fitted with a mechanical stirrer. To this mixture was added $\mathrm{NaNO_2}$ (9.9 g, 0.14 mol) slowly to maintain the temperature below 10 °C. A white solid precipitated during the process. The mixture was left in the ice bath for an additional 30 min, and at room temperature for 4 h. Ether (150 cm^3) and water (20 cm^3) were poured into the flask, and the organic layer was separated and used in the next reaction without further treatment. To the ether solution in a round-bottom flask (500 cm^3) was added ice water (200 g), followed by zinc dust (15 g, 0.23 mol) while stirring for 5 min. The gray Zn dust gradually disappeared accompanied by a temperature rise (to 35−40 °C), and the mixture eventually became a clear solution. At room temperature and without further separation, benzoyl chloride (13.4 cm^3) was added to the flask in three portions with vigorous stirring. A clear greenish liquid was obtained after the mixture was stirred at room temperature for 2 h. Chloroform (250 cm^3) was added to the flask and stirred. The chloroform layer was separated, washed with 10% aqueous $\mathrm{NaHCO_3}$ (2 × 70 cm^3) and water (100 cm^3) to reach a final pH value of 7, and then dried over $\mathrm{Na_2SO_4}$ overnight. Removal of solvent afforded compound **1** as pale yellow crystals (30.7 g, 86%). In a round-bottom flask, fitted with a condenser, a mixture of compound **1** (14.5 g, 0.047 mol), benzene (90 cm^3), and $\mathrm{POCl_3}$ (25 cm^3) was heated using a water bath. HCl gas was evolved when the bath temperature reached 85 °C. This bath temperature was maintained for 10 h until no further HCl gas was evolved. The mixture was poured into ice−water and the benzene layer separated. The aqueous layer was further extracted with benzene (2 × 50 cm^3). The benzene solutions were combined; washed with water (2 × 70 cm^3), 10% aqueous $\mathrm{NaHCO_3}$ (2 × 70 cm^3), and water again (2 × 70 cm^3); and then dried over $\mathrm{Na_2SO_4}$. Removal of solvent afforded compound **2** as an orange liquid (11.8 g, 83%). In a round-bottom flask, compound **2** (5.7 g, 0.019 mol) was dissolved in ethanol (150 cm^3). To this solution was added $\mathrm{NaBH_4}$ (7.3 g, 0.19 mol) over a 5 min period. The mixture was then heated at 70 °C for 1.5 h. At the end of the reaction, water (100 cm^3) and dichloromethane (100 cm^3) were poured into the mixture. The dichloromethane layer was separated, washed with water (2 × 50 cm^3), and dried over $\mathrm{Na_2SO_4}$. Removal of solvent afforded crude title compound **3** as yellow crystals. Colorless

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Table 1. Relative Counting Efficiencies for the PPO Derivatives (Concentration = 1×10^{-2} M)

scintillator	solvent	%
PPO	toluene	100
4-HOCH$_2$-PPO	toluene	99
3-ICPS-PPO	toluene	95
4-HOOC-PPO	toluene/1,4-dioxane (2:1 v/v)	96

Table 2. Preparation of Sol−Gel Glasses Covalently Incorporating 4-HOCH$_2$-PPO[a]

	composition of each vial/mmol						
no.[b]	TEOS	EtOH	H$_2$O	AcOH	4-HOCH$_2$-PPO	fracture-free gel	colorless 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

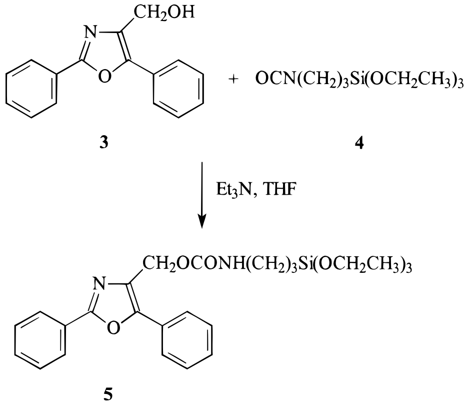
[a] Duplicates of 10 vials were prepared. The mixture was acidic (pH = 3.0). Gelation and aging were carried out at room temperature. The final drying temperature was 70 °C. [b] The same numbering system was used throughout Tables 2−5. Each number refers to the monolithic sol−gel glasses, which were prepared in the same batch with identical PPO concentration.

crystals were obtained in near quantitative yield (97%) after column chromatography using a 1:1 mixture of ethyl acetate and petroleum ether (40−60 °C) as eluent: mp 127−129 °C; NMR δ_H (300 MHz, CDCl$_3$) 8.08 (m, 2H), 7.73 (m, 2H), 7.40 (m, 6H), 4.87 (s, 2H); NMR δ_C (75 MHz, CDCl$_3$) 159.9, 147.3, 136.2, 130.4, 128.8, 128.7, 128.5, 127.9, 126.9, 126.5, 126.3, 56.9.

Preparation of ICPS−PPO adduct (5). A mixture of 4-hydroxymethyl-2,5-diphenyloxazole **3** (2.7 g, 10.7 mmol), 3-isocyanatopropyltriethoxysilane (3.2 g, 12.9 mmol), and triethylamine (1 cm^3) in THF (50 cm^3) was refluxed under nitrogen (Scheme 2). The reaction was closely followed by infrared spectroscopy to monitor the disappearance of the peak at 2273 cm^{-1} (−N=C=O), and the formation of the peak at 1723 cm^{-1} (urethane). At the end of the reaction, removal of THF afforded a crude yellow solid. A near white waxy solid (4.8 g, 87%) was obtained after purification using column chromatography (silica gel, 1:1 mixture of ethyl acetate and petroleum ether 40−60 °C as eluent): mp 53−58 °C; NMR δ_H (300 MHz, CDCl$_3$) 8.11 (m, 2H), 7.75 (m, 2H), 7.47 (m, 6H), 5.28 (s, 2H), 3.82 (q, 6H), 3.22 (m, 2H), 1.60 (m, 2H), 1.23 (t, 9H), 0.63 (m, 2H); NMR δ_C (75 MHz, CDCl$_3$) 160.2, 158.1, 148.8, 132.1, 130.5, 129.0, 128.9, 128.7, 127.7, 127.1, 126.4, 126.2, 50.4, 50.2, 43.5, 23.3, 18.2, 7.6; IR ν_{max} (KBr, cm^{-1}) 1723 (s, −OCONH−). Calcd for $C_{26}H_{34}N_2O_6Si$: C 62.63, H 6.87, N 5.62. Found: C 62.25, H 7.3, N 5.58,

Preparation of Sol−Gel Glasses Incorporating Covalently Bonded 4-HOCH$_2$-PPO. Typically a mixture of TEOS (14.9 cm^3, 67.0 mmol), water (2.4 cm^3, 134.0 mmol), ethanol (11.8 cm^3, 201.0 mmol), and acetic acid (0.85 cm^3, 14.9 mmol) was obtained as a clear, colorless solution (TEOS stock). Five vials (glass, 20 cm^3), each containing 1.5 cm^3 of the TEOS stock, were prepared as samples no. 1 (see Table 2). To the TEOS stock (13.13 cm^3) was added ICPS−PPO adduct **5** (0.12 g, 0.24 mmol), and portions of the solution (5×1.5 cm^3) were withdrawn to give samples no. 4. To the remaining (5.63 cm^3) solution was added the TEOS stock (5.65 cm^3), and portions of the solution were withdrawn (5×1.5 cm^3) to give samples no. 3. To the remaining solution (3.75 cm^3) was added the TEOS stock (3.75 cm^3) again and the mixture placed into five vials (each containing 1.5 cm^3) to give samples no. 2. These vials were sealed with a screw cap then kept at room temperature to gel (1 week) and age (1 week) under ambient conditions. After removal of the cap, the gels were then allowed to dry slowly at room temperature for a further week, followed by drying at 70 °C overnight. Sol−gel glasses were obtained as clear, colorless monoliths.

Scheme 2



Leaching Test. Leaching tests were carried out using UV spectroscopy and XPS to monitor the leachate. For UV monitoring, small monolithic sol−gel glass pieces were added to an UV cell (quartz, 1 cm thick) filled with toluene. The mixture was shaken at regular intervals to mix thoroughly. UV spectra were recorded at different time intervals to obtain the leaching profile of the PPO derivative, while the solids separated from the solution and settled at the bottom of the cell. For XPS analysis, the sol−gel glass disks were packed in a small column, separated by filter papers and thoroughly washed by passing a constant toluene stream that was maintained at a rate of 2 cm^3 min^{-1} through the column. The sol−gel glasses were dried at 70 °C overnight and then mounted on the XPS sample stand using "super glue" prior to analysis.

Liquid Scintillation Counting Procedure To Determine the Relative Counting Efficiency of PPO Derivatives. To a standard glass scintillation vial (20 cm^3) was added 10 cm^3 of a PPO derivative solution (~0.015 M) in toluene as the scintillant. A sample of tritiated water (50 μL) was added to this solution, and the mixture was counted for 2 min to obtain radioactivity, measured as disintegrations per minute (DPM). The counting efficiency was compared with the same HTO sample counted in a standard PPO solution in toluene.

Liquid Scintillation Counting Procedure with the Sol−Gel Glass. To a microvial (0.5 cm^3) was added the stock HTO solution in 1,4-dioxane and solvent (1:2 mixture of ethanol and toluene, 0.4 cm^3) and the coarsely ground sol−gel glass powder (0.07 g). The microvial was then inserted into a standard glass scintillation vial (25 cm^3), and counted for 2 min to obtain the radioactivity.

Results and Discussion

Reaction of 3-Isocyanatopropyltriethoxysilane with 4-HOCH$_2$-PPO. The reaction of 3-isocyanatopropyltriethoxysilane with alcohol is well-known in urethane chemistry. It is catalyzed, for example, by tertiary amines, through a mechanism involving direct attack of the free base on the isocyanate to form the reactive base−isocyanate complex.[23] 1,4-Diazobicyclo[2.2.2]octane (DABCO) was reported to be the most efficient catalyst. Although its catalytic efficiency was only moderate, triethylamine was employed in this work, because it is readily available and it can be easily removed at the end of the reaction. The reaction (Scheme 2), using a slight excess of 3-isocyanatopropyltriethoxysilane, can be followed by infrared spectroscopy, the peak at 2270 cm^{-1} (−NCO) gradually disappearing while the peak at 1723 cm^{-1} (−OCONH−) increases. The final product is very stable and has a long shelf life, which is one of the important general requirements for a liquid scintillation solute.

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Scheme 3

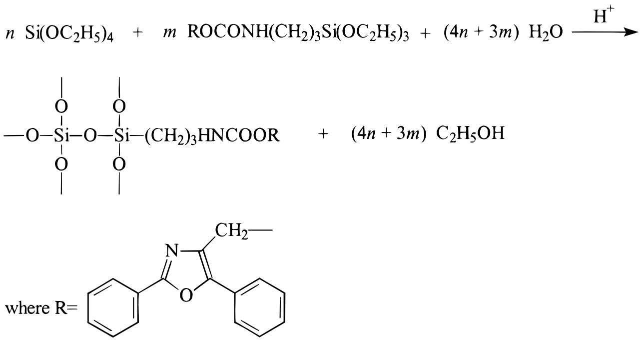

Table 3. BET Surface Area Measurements

no.	degas T (°C)	surface area S ($m^2\ g^{-1}$)	pore V ($cm^3\ g^{-1}$)	av pore d (Å)	isotherm type
1	120	760	0.456	24	IV
2	120	727	0.417	23	IV
3	120	714	0.390	22	IV
4	120	756	0.459	24	IV

Counting Efficiency for Several PPO Derivatives. Table 1 shows that the performance of the 4-functionalized PPO derivatives **3** and **5** as fluor compares well with PPO itself, which is commercially available and the most widely used primary solute. The high efficiency is maintained at the optimum PPO concentration (∼0.015 M). These molecules function effectively as scintillators in the presence of other chemical functionalities, such as alcohol, carboxylic acid, and urethane, and no chemical quenching occurred even at a relatively high concentration. It is important to point out that any colored impurity can significantly reduce the counting efficiency.

Sol−Gel Chemistry. The system containing TEOS/ethanol/water/acetic acid (see Table 2) was used. 3-ICPS-PPO **5** was completely soluble in this mixture, and a clear solution was obtained. Ethanol, which is a reaction byproduct, is not only a solvent for both water and TEOS but also produces a final material which is transparent, suggesting a homogeneous product. Other solvents, such as THF or 1,4-dioxane, failed to provide these advantages. The general sol−gel chemistry is illustrated in a simplified form in Scheme 3. Gelation took place within 3−4 days at room temperature and occurred at a slightly higher rate compared to the case where simple entrapment of PPO was studied. To avoid fracture, the gels were aged at room temperature for a week, while the vials containing the gels were kept tightly closed to avoid the loss of solvent. After aging, the lids were removed and the gels were dried in two stages: first at room temperature, with around 5% (w/w) weight loss per day, for 1 week. Transparent monolithic sol−gel glasses were obtained after further drying at 70 °C overnight, and all operations were carried out under normal atmosphere. As a result 4-$HOCH_2$-PPO is chemically bonded into the SiO_2 network.

Surface Area and Pore Size. Surface area and pore size data are summarized in Table 3. 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 analyzer uses the gas sorption method; the inert gas adsorbate is nitrogen. The BET 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 minimize 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%.[24] The covalently modified sol−gel samples have very similar high surface area and pore diameter values, and they all display a type IV absorption isotherm as classified in the literature,[25] indicating pores in the range of mesopores, which compares well with the average pore diameter. The results suggest that the concentration of 3-ICPS-PPO **5** ($\sim 2 \times 10^{-2}$ M) was too low to affect the sol−gel process. The flexibility of the urethane linkage and the size of the PPO molecule do not affect the physical properties of these sol−gel glasses. These findings are similar to those obtained from the simple entrapment of PPO in the sol−gel glass—no evidence of a template effect was found.

Table 4. XPS Analysis of Selective Covalently Modified Sol−Gel Glasses before and after Treatment in Toluene

	before (atom %)				after (atom %)			
no.	C	O	Si	N	C	O	Si	N
2	17.3	62.3	18.7	1.6	12.0	70.3	16.6	1.0
3	13.7	68.4	16.8	1.1	10.6	70.4	17.6	1.4

Leaching. PPO was reported to display a high-intensity absorption band in the 300−335 nm region due to the $\pi-\pi^*$ conjugate transition in the aromatic structure. In cyclohexane solution fine structure of this absorption band is recognizable. It exhibits peaks at 302 and 318 nm and shoulders at 310 and 333 nm.[26] In toluene, 4-$HOCH_2$-PPO (at 1×10^{-4} M) also displays a very similar absorption band with peaks at 307 and 319 nm, plus shoulders at 311 and 335 nm. The lone pair of electrons on the oxygen of the side chain are too remote from the aromatic system to have a bathochromic effect. The presence of impurities, any volatile residue, such as solvent (ethanol), catalyst (acetic acid), or unreacted starting materials (water, TEOS) was previously shown to have no effect on the UV spectra.[12]

The increase in the absorbance in the UV spectra of a covalently modified sol−gel glass extraction in toluene reflects the increased PPO moiety concentration leached from sol−gel glasses in a semiquantitative manner. However, the amount of PPO moiety leached out from the sol−gel matrix represents only <2% of the total PPO concentration. XPS analysis (Table 4) of the sol−gel glasses before and after washing with toluene showed that the surface nitrogen concentration did not decrease. The result clearly indicates that the 4-$HOCH_2$-PPO concentration at the sol−gel glass surface is not reduced, i.e. the urethane linkage was stable under various conditions to which the samples had been subjected. This point was also confirmed by the ^1H NMR analysis of a $CDCl_3$ extract of the sol−gel glass. In the ^1H NMR spectrum, peaks associated with the aromatic and oxazole rings are visible but the peak characteristic of

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(24) *Coulter SA3100 Series Surface Area and Pore Size Analyser Product Manual*; Coulter Corporation: Miami, Florida, 1996.

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Table 5. Relative Counting Efficiencies of Covalently Modified Sol−Gel Glasses in an Ethanol/Toluene Mixture Compared to a Toluene-Based Scintillator (3.4 g dm^{-3} PPO)

no.	without treatment (%)	heated at 120 °C under vacuum (%)	toluene washed (%)	chloroform washed (%)
1	0	0	0	0
2	45	47	87	73
3	55	56	98	66
4	72	73	96	77

the $-CH_2OH$ chain at 5.28 ppm was markedly absent. It is reasoned that these leached out molecules may be impurities, structurally similar to PPO. In contrast the PPO-doped sol−gel glass obtained through simple entrapment showed that PPO had leached out in toluene (by UV detection), and the sol−gel glass was free of nitrogen after washing with toluene (by XPS analysis). Both results clearly indicate the loss of PPO from the sol−gel glass cages.

Liquid Scintillation Counting Using Sol−Gel Glasses Incorporating Covalently Bonded PPO. The relative efficiency of the sol−gel glasses containing covalently bonded PPO to detect β^- radioactivity from tritiated water (HTO) was investigated using a liquid scintillation counting method. The results are shown in Table 5, and the counting efficiency was compared with that of a standard PPO solution in toluene. Many of the same principles applicable to PPO doped sol−gel glasses from simple entrapment[12] are also applicable to the present samples. Thus, adjustment of the scintillation cocktail, in this case by adding ethanol to suppress the surface H−T exchange or preferential absorption, is still needed and a high efficiency can be achieved. As seen from Table 5, no scintillation process took place and no photons were counted without the PPO moiety being attached to the sol−gel glass. Covalently incorporated PPO can withstand vacuum (up to 10^{-2} mmHg) and high temperature (120 °C), or constant washing with solvent, and the counting efficiency of these sol−gel glasses is not reduced in any way. Although it is observed that counting immediately after mixing gave a somewhat lower DPM value, which might arise from surface exchange[27] or diffusion,[28] within 1 h the DPM reading from the liquid scintillation counter became constant. Other factors, such as the geometry of the sensor and the composition of the glass, may also affect the counting efficiency. Nevertheless, the results clearly demonstrate the suitability of the sol−gel glasses, covalently bonded to a PPO moiety, as sensor materials for detecting β^- radioactivity.

Conclusion

The scintillator primary solute, PPO, has been successfully incorporated via covalent bonding into a porous silica glass, using the sol−gel process. Compared to the physically entrapped scintillator system, leaching of scintillator is significantly reduced. The sol−gel glasses were found to be highly efficient detectors of β^- radioactivity.

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