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# The preparation of polymer beads by photocationic suspension co-polymerisation of 2-(arylsilyl)ethyl vinyl ethers

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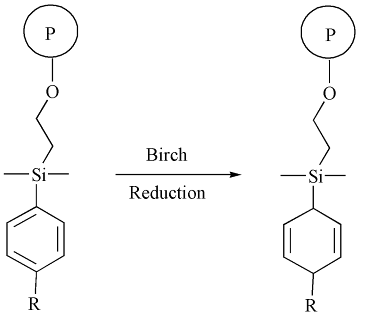
***Received (in Cambridge, UK) 12th February 2002, Accepted 9th July 2002***
***First published as an Advance Article on the web 3rd September 2002***

Polymer beads have been prepared by photocationic suspension polymerisation of 2-(aryldimethyl)silyl ethers in perfluorooctane in the course of our studies on polymer-supported desymmetrisation of 1-silacyclohexa-2,5-dienes. Good yields of 100–200 μm beads of satisfactory shape have been obtained using a perfluorinated co-polymer as stabilising agent. These beads have no permanent porosity although they have a high nominal cross-linking level. Their swelling in common organic solvents is comparable with those of Merrifield or TentaGel gel-type resins.

## Introduction

Solid-phase chemistry is classically performed using gel-type or macroporous polystyrene beads.[1] The polystyrene backbone is generally inert for the majority of reactions involved in polymer-supported synthesis. However, for some applications including Birch reduction of arenes or Friedel–Crafts reactions, the presence of aromatic rings on the support might be troublesome.

We recently reported on the desymmetrisation of 1-silacyclohexa-2,5-dienes as a straightforward route to optically active sugar mimics having potent glycosidase inhibitory activity.[2] Such dienes are easily available through Birch reduction of the corresponding arylsilanes. In order to simplify the purification steps in the event of the development of a combinatorial approach, we envisioned extension of the strategy to solid-phase chemistry using a polymer supported 1-silacyclohexa-2,5-diene (Scheme 1). We thus initiated a study on the preparation of polymer-supported arylsilanes and their modification onto the corresponding diene through Birch reduction. The silicon atom, located between the support and the aromatic ring, would be used both as an orientating group for the Birch reduction[3] and as a 'traceless linker'.[4a] The silylethoxy group frequently used in silicon protective groups[4b] (*i.e.* SEM group) would constitute a suitable and robust linker, which should be easily removed through a fluoride mediated β-elimination. The resulting fluorosilane would then be further oxidised into the corresponding hydroxy group through the Tamao–Kumada–Fleming oxidation. As we needed a non-styrenic polymer support for our purpose, we reasoned that vinyl ether would be an attractive monomer because: i) a poly(vinyl ether) is quite stable towards chemical reaction, ii) functional vinyl ethers are generally easy to synthesise and iii) vinyl ethers, well known to homopolymerise very slowly under radical conditions,[5] are prone to polymerize under cationic conditions.[6] It is obvious that, in this case, the classical aqueous suspension polymerisation cannot be used and therefore an anhydrous system should be developed in order to obtain the desired poly(vinyl ether) supports in a bead shape.



**Scheme 1** Polymer supported Birch reduction of an arylsilane.

In this paper, we report our preliminary studies on the synthesis of organosilyl-functionalised vinyl ethers and their co-polymerisation in suspension with divinyl ether cross-linkers in order to obtain an insoluble polymer support.

## Results and discussion

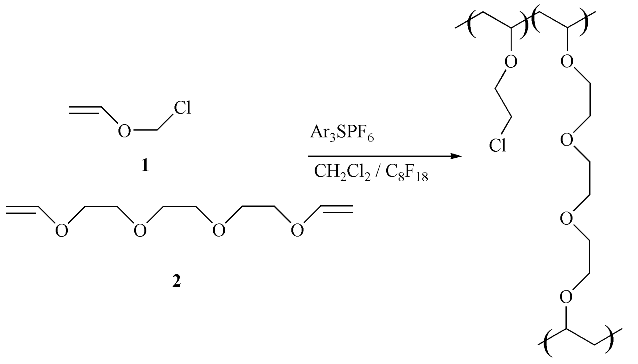
Polymeric supports are generally prepared in bead shapes by suspension polymerisation.[7] This method allows the obtention of spherical particles in the diameter size range of 100–500 μm, the most suitable for applications in solid-phase supported chemistry. In the vast majority of examples of suspension polymerisation reported in the literature, the suspending medium is an aqueous solution containing a stabilising agent,[8] whereas the dispersed droplets contain a mixture of hydrophobic co-monomers and a radical initiator. In the case of the preparation of polymeric beads from hydrophilic monomers such as acrylic acid, the so-called inverse suspension polymerisation has to be used.[9] In this case, the suspending medium is generally paraffin oil, but low-boiling organic solvents were also used,[10] the hydrophilic co-monomers being then dispersed as an aqueous solution. Obviously, the presence of water precludes the use of anionic or cationic polymerisation systems. The system must meet with several requirements which are difficult to combine: i) the two phases involved should be completely immiscible at the temperature used for the polymerisation, ii) the monomer has to be liquid in order to form homogeneous droplets whereas it has to be completely insoluble in the continuous medium, iii) an efficient stabilising agent has to be found in order to avoid agglomeration of the polymerising phase and to allow the obtention of spherical beads and iv) the polymerisation should initiate only when a stable suspension of droplets of the right size is obtained. Following the work of pioneers,[11] Meldal and co-workers have developed the concept of non-aqueous suspension polymerisation using silicone oil as a continuous medium.[12] In order to generalise their approach, they have synthesised a new kind of surfactant allowing the preparation of a large range of PEG-based resins by anionic or cationic ring-opening polymerisation.[13] The different beaded

DOI: 10.1039/b201520j

supports thus obtained were successfully used in solid-phase synthesis.[14] However, even if silicone oil is a good suspending medium for hydrophilic PEG-containing monomers, the solubility of other kinds of compounds in low-viscosity silicone oil is not always negligible.[15] In these cases, a truly non-solubilising medium is required. Perfluorocarbon solvents are a very attractive alternative for this purpose. The use of a perfluorocarbon solvent as the suspending medium in suspension polymerisations was proposed by Zhu[16] and Mosbach and co-workers[17] in their pioneering works. This approach appeared attractive since perfluorocarbons are highly insoluble with non-fluorinated organic compounds near or below ambient temperature.[18] The perfluorocarbon used in this study was the perfluorooctane.

## 1. Optimisation of the suspension polymerisation conditions

We started our study by searching for the optimal conditions needed to obtain regular spherical beads with the 2-chloroethyl vinyl ether **1**–tri(ethylene glycol) divinyl ether **2** system (Scheme 2). Our first attempt was realised with $BF_3\cdot Et_2O$ as a polymerisation catalyst[19] and sodium dodecylsulfonate as a stabiliser. The suspension polymerisation device which we used has previously been described.[20] The polymerisation was very rapid, even at −70 °C, and the polymer was collected as a black powder on the walls of the reactor without formation of beads. Obviously, we had to find a more efficient stabiliser as well as more practical polymerisation conditions.

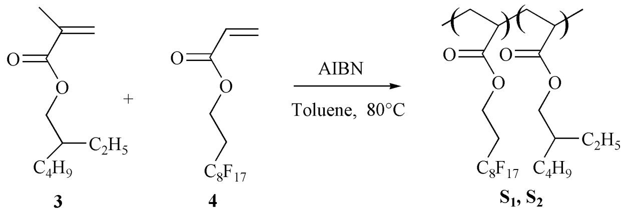


**Scheme 2** Photocationic suspension co-polymerisation of 2-chloroethyl vinyl ether with tri(ethylene glycol) divinyl ether.

Crivello *et al.*[21] have described a photoinitiated cationic polymerisation of vinyl ethers. In our case, such an approach would allow us to set up good suspension conditions at room temperature before the initation of the polymerisation by irradiation. The exothermicity developed by the reaction should be absorbed by the large excess of continuous phase. Commercially available triaryl sulfonium hexafluorophosphonate was chosen as the catalyst and perylene was added to initiate the photolysis of the triarylsulfonium salt in the visible region.[22]

In order to avoid aggregation of the forming beads, the stabiliser should be soluble in the continuous phase (*i.e.* the perfluorooctane) but still be able to interact with the dispersed droplets of monomer. In our case, the ideal stabiliser should constitute a convenient balance of a perfluoro-alkylated component and a perhydro-alkylated part. Having failed to obtain satisfactory results with the commercially available perfluorohexyldecene, we decided to synthesise our own stabiliser.

Based on the pioneering work of Mosbach and co-workers[17] we reasoned that a co-polymer of perfluoroacrylate and a methacrylate would lead to an efficient stabilising agent.



**Scheme 3** Synthesis of the perfluorinated emulsifying agents $S_1$ and $S_2$.

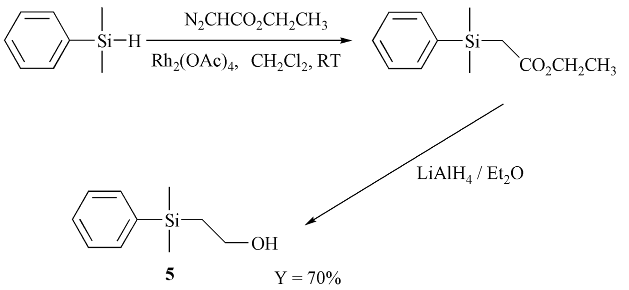
**1.1 Synthesis of the stabilising agent.** Co-polymers of 2-ethylhexyl methacrylate **3** and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate **4**[23] were synthesised by radical polymerisation using two different molar ratios (Scheme 3). The results of the polymerisation have been summarized in Table 1. The co-polymer composition is very similar to that of the monomer feed. This behavior is in good agreement with previously published results with closely related systems.[24]

**1.2 Test of the efficiency of the stabilisers.** The ability of the two co-polymers obtained above to act as stabilising agents of an organic–perfluorocarbon suspension was tested with our system. Our results are reported in Table 2. While aggregation still appears with the weakly fluorinated stabiliser $\mathbf{S_1}$, the use of the more highly fluorinated $\mathbf{S_2}$ at its higher possible concentration allows the obtention of satisfactory yields of spherical beads. Therefore, $\mathbf{S_2}$ at a concentration of 0.15% (w/v) was used for all the following experiments.

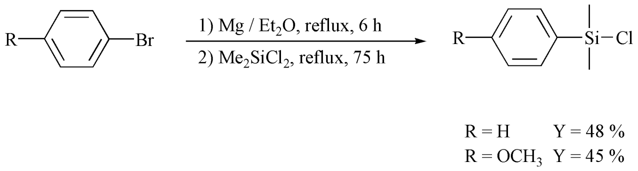
## 2. Synthesis of the organosilyl vinyl ethers

Different synthetic routes may be envisioned to obtain these compounds. However, in each case the key intermediate is the 2-(aryldimethylsilyl)ethanol which will give access to the desired product by transetherification.

**2.1 Preparation of 2-(dimethylphenylsilyl)ethanol 5.** 2-(Dimethylphenylsilyl)ethanol **5** was obtained through reduction of an α-silyl ester prepared in one step by $Rh_2(OAc)_4$ catalyzed insertion of ethyl diazoacetate into the Si–H bond of $PhMe_2SiH$.[25] The fragile α-silyl ester was not isolated but directly reduced into the desired alcohol **5** in 70% overall yield (Scheme 4). In parallel, we developed an alternative procedure allowing the large scale preparation of our precursors and the possible extension to the synthesis of diversely substituted analogues. Compound **5** was thus available starting from $PhMe_2SiCl$ (Scheme 5) using a Reformatski reaction, followed by reduction of the ester function of the α-silyl ester with $LiAlH_4$ (Scheme 6). It is noteworthy that the use of ether as a co-solvent in the Reformatski reaction was essential in order to



**Scheme 4** Synthesis of 2-(dimethylphenylsilyl)ethanol **5** through rhodium–carbene insertion.



**Scheme 5** Synthesis of aryldimethylchlorosilanes.

**Table 1** Synthesis of the stabilizers

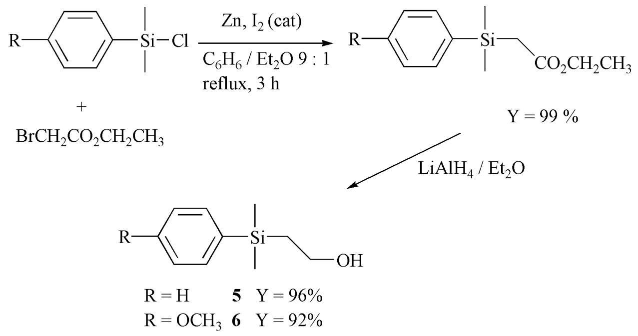
| Resulting stabiliser | Monomer feed composition (mol%) 3 | Monomer feed composition (mol%) 4 | Co-polymer composition[a] (mol%) 3 | Co-polymer composition[a] (mol%) 4 | Yield of co-polymer(%) | Fluorine loading[a] (%, w/w) |
|---|---|---|---|---|---|---|
| **$S_1$** | 0.7 | 0.3 | 0.75 | 0.25 | 83 | 33 |
| **$S_2$** | 0.5 | 0.5 | 0.54 | 0.46 | 78 | 44 |

[a] Estimated from elemental analysis (F).

**Table 2** Efficiency of the stabiliser in the photocationic suspension co-polymerisation

| Entry | Monomer feed composition (mol%) 1 | Monomer feed composition (mol%) 2 | Chlorine loading of the co-polymer/mmol g$^{-1}$ Expected[a] | Chlorine loading of the co-polymer/mmol g$^{-1}$ Obtained[b] | Stabiliser used (%, w/v) | Co-polymer aspect | Yield of polymer in satisfactory bead shape (%) |
|---|---|---|---|---|---|---|---|
| **1** | 0.5 | 0.5 | 6.5 | 5.7 | **$S_1$** (0.1) | Aggregation | — |
| **2** | 0.5 | 0.5 | 6.5 | 5.6 | **$S_2$** (0.1) | Aggregation + some beads | 15 |
| **3** | 0.5 | 0.5 | 6.5 | 5.2 | **$S_2$** (0.15)[c] | Beads + some aggregation | 85 |

[a] Calculated from the monomer feed composition. [b] Estimated from elemental analysis (Cl). [c] Maximum apparent solubility.



**Scheme 6** Synthesis of 2-(aryldimethylsilyl)ethanols **5** and **6** *via* the Reformatski reaction.

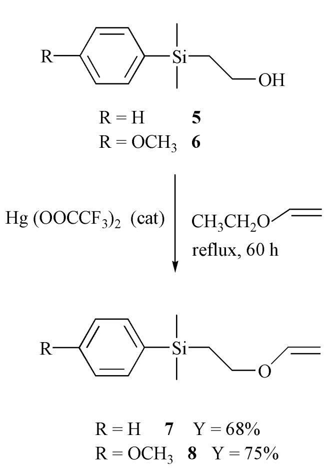
obtain acceptable yields of α-silyl esters.[26] The use of benzene alone led to poor results due to the aggregation and thus to the low reactivity of the zinc reagent in this solvent. Accordingly, analogue **6** was prepared using the same route, starting from 4-methoxyphenyldimethylchlorosilane, available from the corresponding aryl bromide[27] as depicted in Scheme 5. Analogue **6** was prepared since it was envisioned that such arylsilanes could be versatile precursors for other supported organosilanes. A 4-methoxyphenyl group on silicon can be readily cleaved under electrophilic conditions since electron-donating groups on the aromatic ring are known to dramatically increase the rate of *ipso* substitution of arylsilanes.[28] For instance, *ipso* substitution with HCl would afford the corresponding chlorosilane which would constitute a valuable precursor for various types of supported organosilanes.

**2.2 Transetherification.** The introduction of the vinyl ether function was carried out by transetherification of the silyl alcohol with ethyl vinyl ether using a catalytic amount of $Hg(OOCF_3)_2$ (Scheme 7).[29]

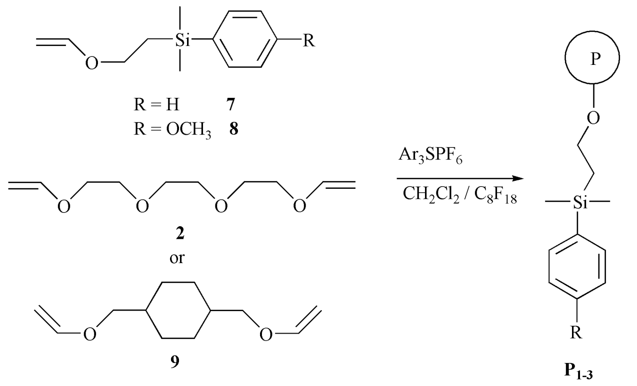
Having our organosilyl vinyl ether monomers in hand, we then studied their photocationic polymerisation in suspension.

## 3. Photocationic suspension polymerisation of the (aryldimethylsilyl)ethyl vinyl ethers

Polymer beads were prepared using **7** and **8** as monomers and tri(ethylene glycol)divinyl ether **2**, or cyclohexane-1,4-dimethanol divinyl ether **9** as cross-linking agents (Scheme 8). Compound **9** was employed in order to increase the rigidity of the resulting beads. The suspension polymerisation conditions used in this case were those established previously for the **1**–**2** system. Our results are summarized in Table 3.



**Scheme 7** Synthesis of 2-(aryldimethylsilyl)ethyl vinyl ethers **7** and **8**.



**Scheme 8** Preparation of supports **$P_1$** to **$P_3$** by photocationic suspension co-polymerisation.

Good yields of beads having a spherical shape were obtained using both cross-linkers. The resulting polymers **$P_{1-3}$** are soft light-orange colored beads in the diameter range 800–200 µm (Fig. 1).

## 4. Structural characterisation of supports $P_{1-3}$

**4.1 Specific surface area.** Specific surface areas of our different supports were measured using the nitrogen adsorption

**Table 3** Photocationic suspension co-polymerisation of the organosilyl monomers

| Entry | Monomer feed composition (mol%) | | Silicon co-polymer loading/mmol $g^{-1}$ Expected[a] | Obtained[b] | Beads aspect | Yield of polymer in satisfactory bead shape (%) |
|---|---|---|---|---|---|---|
| $\mathbf{P_1}$ | **7** (0.5) | **2** (0.5) | 4.6 | 3.7 | Some aggregation | 75 |
| $\mathbf{P_2}$ | **7** (0.5) | **9** (0.5) | 4.9 | 4.8 | Beads + little aggregation | 82 |
| $\mathbf{P_3}$ | **8** (0.5) | **2** (0.5) | 4.6 | 3.5 | Beads + little aggregation | 85 |

[a] Calculated from monomer feed composition. [b] Estimated from elemental analysis (Si).

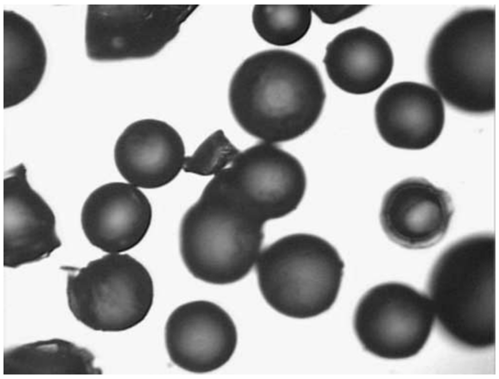


**Fig. 1** Optical microscope photography of $\mathbf{P_1}$ beads.

method through a BET (Brunauer–Emmett–Teller) treatment. The results are as follows: $\mathbf{P_1}$ = 0.08 $m^2$ $g^{-1}$, $\mathbf{P_2}$ = 1.1 $m^2$ $g^{-1}$, $\mathbf{P_3}$ = 1.3 $m^2$ $g^{-1}$. Therefore, it appears that in the dry state, our poly(vinyl ether) polymers have no permanent porosity.

**4.2 Swelling of the supports in solvents.** The degree of swelling of a polymeric support is a good indication of its compatibility with the solvent and therefore, of the ability of small molecules to diffuse towards the polymeric moieties grafted onto the chains.[30] This parameter is even more important for supports having no permanent porosity such as $\mathbf{P_{1–3}}$.

We have mesured the swelling of support $\mathbf{P_1}$ in some common organic solvents and compared them with those reported in the literature for Merrifield gel-type resin and TentaGel S RAM (both 1% DVB cross-liked).[31] The results are summarised in Fig. 2. The range of solvents compatible with supports $\mathbf{P_1}$ is comparable with that of Merrifield resins, but is less extended than for TentaGel. The swelling values are of the same order of magnitude.

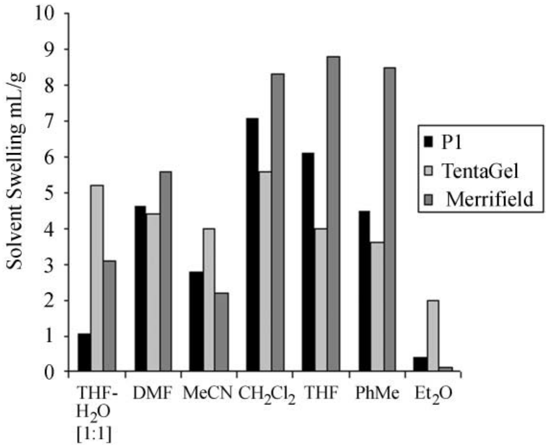


**Fig. 2** Solvent swelling of support $\mathbf{P_1}$ compared with some commercial beads.

## Experimental

### 1. Materials

Triarylsulfonium hexafluorophosphonate (50% solution in propylene carbonate) (Aldrich), perylene (Aldrich), and tri(ethylene glycol) divinyl ether (Aldrich) were used without purification. Perfluorooctane (P.M. fluorochemicals, Moscow, Russia) was distilled ($bp^{760}$ = 103–104 °C) before use. The remaining solvents and chemicals were general purpose reagents. All reactions were performed under a flow of $N_2$.

### 2. Synthesis of the stabiliser $S_2$

Perfluorooctylethyl acrylate **4** (2 mmol, 1.12 g), 2-ethylhexyl methacrylate **3** (2 mmol, 0.396 g) and AIBN (0.04 mmol, 6.6 mg) were placed in a 25 mL Schlenk tube. The system was degassed three times then heated at 80 °C under stirring for 15 h. The resulting gel was then redissoved in ether (100 mL), concentrated under vacuum then precipitated in methanol. A white powder was collected under filtration (1.1 g, yield = 78%). Elemental analysis F: 32.9%.

The same procedure was employed for the synthesis of $\mathbf{S_1}$.

### 3. Synthesis of 2-(dimethylphenylsilyl)ethanol with ethyl diazoacetate

Dimethylphenylsilane (7.14 g, 52.4 mmol) was dissolved in dichloromethane (20 mL) in a 100 mL two-neck round bottom flask. $Rh_2(OAc)_4$ (0.88 g, 2 mmol) was then added. A solution of ethyl diazoacetate (5.74 g, 50.3 mmol) in dichloromethane (40 mL) was then added slowly to the stirred solution at room temperature using a syringe pump at a rate of 1.2 mL $h^{-1}$. When the addition was complete, dichloromethane was evaporated under vacuum and anhydrous ether (50 mL) was added to the residue. A solution of $LiAlH_4$ (1.9 g, 50 mmol) in ether (30 mL) was then added dropwise at 0 °C, over a period of 15 min. The reaction was heated under reflux for 1.5 h, then cooled down to 0 °C in an ice bath and water (30 mL) was added. The organic layer was decanted and the aqueous phase extracted with ether (2 × 50 mL). The combined organic layers were collected, dried over $MgSO_4$, and the solvent evaporated under vacuum. Compound **5** was obtained as an oil (5 g, yield = 70%). $^1$H-NMR $\delta$ ($CDCl_3$) 0.3 (6H, s, $(CH_3)_2Si$), 1.25 (2H, $CH_2Si$), 1.8 (1H, s, OH), 3.7 (2H, m, $CH_2OH$), 7.2–7.45 (5H, Ar). $^{13}$C-NMR $\delta$ ($CDCl_3$) −2.8 ($(CH_3)_2Si$), 21.1 ($CH_3Si$), 59.9 ($OCH_2$), 127.8 (*CH*–CH–*CH*), 129.0 (CH–*CH*–CH), 133.4 (Si–C–*CH*), 138.5 ($(CH_3)_2Si$–*C*). IR ($cm^{-1}$) 3362 (OH), 2956 (C–H), 1425, 1251 (Si–$CH_3$), 1119 (SiAr), 1038, 825, 738 (Ar), 700 (Ar).

### 4. Synthesis of chlorodimethyl(4-methoxyphenyl)silane

In a 100 mL two-neck round bottom flask, magnesium turnings (5.24 g, 222 mmol) were placed in anhydrous ether (30 mL). A solution of 4-bromoanisole (31.8 g, 170 mmol) in ether (75 mL) was added dropwise to the suspension, over a period of 1 h. The reaction mixture was then heated under reflux for 6 h, and then cooled in an ice bath. A solution of dichlorodimethylsilane (25.8 g, 200 mmol) in ether (40 mL) was added dropwise over a period of 30 min. The reaction mixture was then heated under reflux for 80 h. After cooling, the resulting thick suspension was filtered over Celite under vacuum and the solid washed with petroleum ether (2 × 50 mL). The organic layers were collected and concentrated under vacuum. The resulting viscous oil was distilled under reduced pressure in a Kugelrohr apparatus ($bp^{0.6}$ = 82 °C), to give a light-orange oil (13.6 g, yield = 40%). $^1$H-NMR $\delta$ ($CDCl_3$) 0.6 (6H, s, $(CH_3)_2Si$), 3.7 (3H, s, $CH_3O$), 6.75–6.9 (2H, Ar), 7.2–7.5 (2H, Ar). $^{13}$C-NMR $\delta$ ($CDCl_3$) 2.3 ($(CH_3)_2Si$), 55.1 ($OCH_3$), 113.9 ($CH_3O$–C–CH), 121.1 (Si–C–*CH*), 124.9 ($(CH_3)_2Si$–*C*), 134.8 ($CH_3$–O–*C*). IR ($cm^{-1}$) 2963 (C–H), 1599 (Ar), 1498 (Ar), 1248 (Si–$CH_3$), 1114 (Si–Ar), 1077, 1041, 808, 767 (Ar).

## 5. Synthesis of ethyl 2-[dimethyl(4-methoxyphenyl)silyl]ethanoate

Zinc powder (acid-washed) (3.5 g, 50 mmol), was suspended in dry benzene (55 mL) in a 250 mL three-necked round bottom flask equiped with a magnetic stirrer, a condenser and an inlet for nitrogen. An iodine crystal was then added and the suspension gently heated at 40–50 °C under stirring while a solution of chlorodimethyl(4-methoxyphenyl)silane (8.5 g, 42.4 mmol) and ethyl bromoacetate (8.81 g, 52.7 mmol) in a mixture of benzene (12 mL) and ether (12 mL) was added dropwise over a period of 1 h. The reaction mixture was then heated under reflux for 2.5 h. After cooling the flask in an ice bath, a solution of hydrochloric acid (1 mol $L^{-1}$, 50 mL) was added dropwise. The organic layer was decanted and the organic phase washed sucessively with HCl (1 mol $L^{-1}$, 50 mL), saturated $Na_2CO_3$ (2 × 50 mL) then water (2 × 50 mL). After drying over $MgSO_4$ and elimination of the solvent under vacuum, a light-yellow oil was obtained (10.7 g, yield = 99%). $^1$H-NMR $\delta$ ($CDCl_3$) 0.2 (6H, s, $(CH_3)_2Si$), 1.2 (2H, t, O–$CH_2$–$CH_3$), 2.0 (2H, s, $CH_2Si$), 3.65 (3H, s, $CH_3O$), 3.9 (2H, t, O–*C*$H_2$–$CH_3$), 6.7–6.9 (2H, Ar), 7.0–7.3 (2H, Ar). $^{13}$C-NMR $\delta$ ($CDCl_3$) −2.4 ($(CH_3)_2Si$), 14.8 (*C*$H_3$–$CH_2$), 25.1 (Si–$CH_2$), 52.0 (O–*C*$H_2$–$CH_3$), 55.1 (O–$CH_3$), 114.1 ($CH_3O$–C–*CH*), 122.0 (Si–C–*CH*), 128.9 ($(CH_3)_2Si$–*C*), 134.8 ($CH_3O$–*C*), 172.1 (C=O). IR ($cm^{-1}$) 2959 (Si–C), 1720 (COOEt), 1596 (Ar), 1504 (Ar), 1464, 1279 (Si–C), 1248 (Si–$CH_3$), 1183, 1114 (Si–Ar), 824, 776 (Ar).

## 6. Synthesis of ethyl [2-(dimethylphenyl)silyl]ethanoate

The title compound was obtained from chlorodimethylphenylsilane according to the same procedure as for ethyl 2-[dimethyl(4-methoxyphenyl)silyl]ethanoate, (yield = 98%). Spectroscopic data were identical in many respects with those described in the literature.[25b]

## 7. Synthesis of 2-[dimethyl(4-methoxyphenyl)silyl]ethanol 6

In a 100 mL two-necked round bottom flask equiped with a magnetic stirrer, a condenser and an inlet for nitrogen, a solution of ethyl 2-[dimethyl(4-methoxyphenyl)silyl]ethanoate (10.7 g, 42 mmol) in ether (100 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (1.7 g, 45 mmol) in anhydrous ether (55 mL). The reaction mixture was then heated under reflux for 1.5 h. After cooling in an ice bath, water (50 mL) was added dropwise and the layers were decanted. The aqueous phase was washed with ether (2 × 50 mL). The organic phases were collected, dried under $MgSO_4$, and the solvent evaporated under vacuum. Compound **6** was obtained as an oil (8.55 g, yield = 96%). $^1$H-NMR $\delta$ ($CDCl_3$) 0.2 (6H, s, $(CH_3)_2Si$), 1.2 (2H, $CH_2Si$), 1.8 (1H, s, OH), 3.45 (2H, $CH_2O$), 3.6 (3H, s, $CH_3O$), 6.5–6.8 (2H, Ar), 7.0–7.3 (2H, Ar). $^{13}$C-NMR $\delta$ ($CDCl_3$) −2.4 ($(CH_3)_2Si$), 21.2 ($CH_3Si$), 59.7 ($OCH_2$), 127.5 (*CH*–CH–*CH*), 134.2 (Si–C–*CH*), 135.1 ($CH_3O$–Si), 138.1 ($(CH_3)_2Si$–*C*). IR ($cm^{-1}$) 3363 (OH), 2958 (C–H), 1595 (Ar), 1503 (Ar), 1463, 1277 (Si–C), 1250 (Si–$CH_3$), 1112 (Si–Ar), 1033, 823, 780 (Ar).

## 8. Synthesis of 2-(dimethylphenylsilyl)ethanol 5

The title compound was obtained from ethyl 2-dimethylphenylsilyl ethanoate using the same procedure as for 2-[dimethyl-(4-methoxyphenyl)silyl]ethanol (yield = 96%).

## 9. Synthesis of 2-(dimethylphenylsilyl)ethylvinyl ether 7

In a 500 mL three-necked round bottom flask equipped with a thermometer, a dropping funnel and a septum, was placed a solution of 2-(dimethylphenylsilyl)ethanol **5** (6.6 g, 40 mmol) in ethyl vinyl ether (200 mL). Triethylamine (0.56 mL, 4 mmol), then mercury trifluoroacetate (0.856 g, 2 mmol) in ethyl vinyl ether (5 mL) were then sucessively added to the stirred suspension. The reaction mixture was heated under reflux for 60 h. After cooling to room temperature, a 2 M solution of NaOH (50 mL) was added dropwise with stirring. The organic layer was decanted and the aqueous phase extracted with ether (3 × 50 mL). The combined organic layers were collected and successively washed with saturated solutions of $NaHCO_3$ (50 mL), $NH_4Cl$ (50 mL) and NaCl (50 mL). After drying over $MgSO_4$, the solution was concentrated under vacuum to give a viscous oil. Kugelrhor apparatus distillation under reduced pressure ($bp^{0.8}$ = 70 °C), gave compound **7** as a yellow oil (5.1 g, yield = 62%). $^1$H-NMR $\delta$ (250 MHz, $CDCl_3$) 0.35 (6H, s, $(CH_3)_2Si$), 1.10 (2H, t, *J* = 8.1 Hz, $CH_2Si$), 3.70 (2H, t, *J* = 8.1 Hz, $CH_2$*C*$H_2$O), 3.80 (2H, t, *J* = 8.1 Hz, O*C*$H_2$CH), 4.05 (1H, dd, *J* = 6.8, 1.8 Hz, OCH=C*H*$_2$), 4.20 (1H, dd, *J* = 14.4, 1.8 Hz, OCH=C*H*$_2$), 6.5 (1H, dd, *J* = 14.4, 6.8 Hz, OC*H*=$CH_2$), 7.55–7.65 (5H, Ar). $^{13}$C-NMR $\delta$ (90 MHZ, $CDCl_3$) −02.5 ($(CH_3)_2Si$), 16.9 (Si–$CH_2$), 65.3 (Si–$CH_2$–*C*$H_2$O), 86.8 (O–*C*H=$CH_2$), 114.5 (–C–*C*H), 121.0 (Si–C–*C*H), 152.1 (*C*$H_2$=CH–O). IR ($cm^{-1}$) 2956 (C–H), 1636 (OCH=$CH_2$), 1614 (OC=$CH_2$), 1596 (Ar), 1504 (Ar), 1318 (Si–C), 1248 (Si–$CH_3$), 1182 ($OCH_2$=$CH_2$), 1112 (Si–Ar), 823, 778 (Ar). Found C 64.8; H 8.2; Si 12.3. $C_{12}H_{18}OSi$ requires C 64.9; H 8.1; Si 12.6%.

## 10. Synthesis of 2-[dimethyl(4-methoxyphenyl)silyl]ethyl vinyl ether 8

The title compound was obtained from 2-[dimethyl-(4-methoxyphenyl)silyl]ethanol **6** using the same procedure as for 2-(dimethylphenylsilyl)ethyl vinyl ether **7** (yield = 75%). $^1$H-NMR $\delta$ ($CDCl_3$) 0.35 (6H, s, $(CH_3)_2Si$), 1.25 (2H, t, *J* = 8.0 Hz, $CH_2Si$), 3.70 (2H, t, *J* = 8.1 Hz, $CH_2$*C*$H_2$O), 3.80 (2H, t, *J* = 8.0 Hz, O*C*$H_2$CH), 3.85 (3H, s, $CH_3O$), 3.95 (1H, dd, *J* = 6.5, 2.1 Hz, OCH=C*H*$_2$),.4.15 (1H, dd, *J* = 14.2, 1.7 Hz, OCH=C*H*$_2$), 6.45 (1H, dd, *J* = 14.2, 6.5 Hz, OC*H*=$CH_2$), 6.9–7.0 (2H, Ar), 7.45–7.55 (2H, Ar). $^{13}$C-NMR $\delta$ (90 MHZ, $CDCl_3$) −0.25 $(CH_3)_2Si$), 17.1 (Si–$CH_2$), 55.0 ($OCH_3$), 65.5 (Si–$CH_2$–*C*$H_2$O), 86.5 (O–*C*H=$CH_2$), 113.8 ($CH_3O$–C–*C*H), 121.0 (Si–C–*C*H), 129.1 $(CH_3)_2Si$–*C*), 135.0 ($CH_3O$–*C*), 151.7 (*C*$H_2$=CH–O). IR ($cm^{-1}$) 2956 (C–H), 1636 (OCH=$CH_2$), 1614 (OC=$CH_2$), 1596 (Ar), 1504 (Ar), 1318 (Si–C), 1248 (Si–$CH_3$), 1182 ($OCH_2$=$CH_2$), 1112 (Si–Ar), 823, 778 (Ar). Found C 66.2; H 8.3; Si 11.6. $C_{13}H_{20}OSi$ requires C 66.1; H 8.5; Si 11.9%.

## 11. Suspension polymerisation

The supports were prepared using a non-aqueous suspension polymerisation using a parallel-side flanged glass reactor specially designed according to the literature.[7]

In a typical experiment, the suspension medium was prepared by dissolving the stabiliser $\mathbf{S_2}$ (330 mg) in perfluorooctane (200 mL) under mechanical stirring (500 rpm) over 1 h. The speed was then reduced to 250 rpm, and a mixture of tri(ethylene glycol) divinyl ether **2** (0.92 g, 4.55 mmol), 2-(dimethylphenylsilyl)ethyl vinyl ether **7** (0.83 g, 4.55 mmol), hexafluorophosphonium triarylsulfonium (140 µL) and perylene (10 mg, 0.4 mmol) in dichloromethane (1.8 mL) was added rapidly. The stirring speed was adjusted (usually between 200–250 rpm) at room temperature in order to obtain, visually, droplets of satisfactory size. A day-light tungsten lamp was then placed at about 5 cm from the wall of the reactor and the suspension irradiated under mechanical stirring for 30 min. The resulting beads were filtered under vacuum, washed with dichloromethane (2 × 100 mL) then continuously extracted for 48 h with THF in a Soxhlet apparatus. After filtration, the beads were sieved manually (0.17 g > 800; 800 < 0.18 g > 500; 500 < 0.37 g > 315; 315 < 0.75 g > 200; 0.28 g < 200 µm) The beads in the diameter range 800–200 µm were collected (1.3 g, 75%), and both the very small and large particles were discarded. Perfluorooctane was regenerated by distillation (190 mL, yield = 90%).

### 12. Solvent swelling determination

The swelling ratio of beads was obtained as follows: about 0.5 g of dry spherical beads (range size 800–200 µm) were accurately weighed into a graduated cylinder (id 10 mm). The apparent volume of the dry material was measured ($V_d$). Solvent was added to the cylinder with gentle shaking to remove every entrapped air. The beads were then allowed to swell without entrapping air bubbles at room temperature for 48 hours and the apparent swollen volume mesured ($V_s$). The swelling volume was given by: $V_s - V_d$.

## Conclusion

This paper describes the efficient preparation of beads by photocationic suspension polymerisation of 2-(aryldimethylsilyl)ethyl vinyl ethers with perfluorooctane as the dispersing medium. Even with a nominal cross-linking level of 50%, the resulting supports have no permanent porosity. In terms of swelling in solvents, these new poly(vinyl ether) supports behave somewhere between Merrifield and TentaGel resins.

Applications of these new supports to solid-phase organic synthesis *via* the Birch reduction of the aryl moiety are currently under investigation.

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