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Thin film format for polymer supports – synthesis and chemical modification

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An easy and convenient method for the preparation of functionalised porous polymer films ($\sim 76 \times 14$ mm) of uniform thickness ($\sim$60–120 μm) has been developed using microscope slides stacked together as a mould for UV-initiated polymerisation of comonomer mixtures. Both gel-type and macroporous styrene and methacrylate-based species have been prepared by appropriate choice of crosslinker (%) and porogen. The incorporation of functional comonomers: 4-vinylpyridine, vinylbenzyl chloride or glycidyl methacrylate allows ready further chemical modification of the films for potential application in a number of areas.

Introduction

Though by far the most used format for polymer supports is the spherical particulate species derived from suspension polymerisation reactions,[1,2] there remains significant interest and value in other formats such as soluble polymers,[3,4] macroscopic porous monoliths,[5,6] pins[7] *etc.* Recently for example we have described a method for the preparation of rods and discs derived therefrom.[8] Though many of these species provide convenience and utility in the particular applications for which they have been devised, in general they are not convenient for example for being probed *via* transmittance spectroscopy. In the course of a recent collaborative project[9] involving real-time *in situ* FTIR mechanistic studies of a polymer-supported metal complex catalysed reaction operated at low pH and high temperature, we have been required to produce the polymer-support in the form of a thin film to allow direct transmittance spectroscopy investigation of the catalytic species attached to the support. We now report the synthesis and chemical modification of such thin film polymer supports.

Results and discussion

Microscope slide mould format

After a number of futile attempts to devise and fill moulds with comonomer mixtures potentially suitable for thin polymer film formation, we realised that two appropriately spaced standard microscope slides (76×26 mm) can be readily filled with a pre-mixed comonomer–porogen–initiator solution by capillary action. Choice of a suitable initiator then allows efficient polymerisation *via* UV/visible light irradiation. Furthermore in our hands up to 9 microscope slides can be clamped together in a single assembly, allowing simultaneous preparation of 8 films (Fig. 1). Pre-treatment of the slides with silicone oil prevents adhesion of the films to the slides, and the former can be peeled gently from the latter if necessary with the aid of a razor blade. With care the films can then be manipulated much as suspension polymer beads and can for example be cleaned by extraction in a Soxhlet apparatus, and used in batch reactions to introduce functionality into the matrix and to perform solid phase synthesis. In our initial project the films have also proved invaluable for our collaborators in performing transmittance FTIR studies as planned on metal complex species attached to the film matrix.

Gel-type films

Gel-type styrene–vinylbenzyl chloride (VBC) films with different crosslinkers and a methyl methacrylate (MMA)–glycidyl† methacrylate (GMA) film crosslinked with ethylene glycol dimethacrylate (EGDMA) were prepared in the absence of any porogen. Using a single thickness of PTFE tape as the spacer yielded films $\sim$60–80 μm in thickness. Two thicknesses of tape allowed films of $\sim$120 μm to be prepared. Microscope slides with a greater gap did not fill completely and uniformly by capillary action. Typical polymerisation mixtures employed are shown in Table 1. All the films were transparent. The styrene–VBC–divinylbenzene (DVB) material, **1**, was brittle in the dry state, and in a good solvent (*e.g.* toluene) swelled to produce a fragile film that fragmented readily due to osmotic shock. All attempts to produce lightly crosslinked gel-type styrene–VBC–DVB films failed in this way. Replacing the DVB with poly(ethylene glycol) α,ω-divinylbenzyl ether (PEG1000 DVBE) or with PEG1500 DVBE,[10–12] as the crosslinker produced much more flexible films, **2** and **3**, even in the dry state (Fig. 2). These swelled significantly in toluene, were not subject to damage by osmotic shock, and with care could be physically manipulated *e.g.* in and out of flasks. The MMA–GMA–EGDMA film, **4**, was only slightly more flexible than the styrene–VBC–DVB species, **1**, and also tended to fragment when treated with swelling solvents. However extensive work in progress with GMA-based films employing PEG-based cross-linkers similar to the PEG DVBE species above has shown that relatively tough and highly flexible films are accessible by this approach.[13]

Chemical modification of gel-type films

To demonstrate the feasibility of chemically derivatising gel-type films the VBC-containing species **1**–**3** were each reacted with 5-bromosalicylic acid methyl ester in the presence of sodium methoxide in dimethylacetamide, as the first step (Scheme 1) in a model solid phase synthesis protocol.[8] Each film was introduced carefully into a 25 ml round-bottomed flask to perform the reaction. After 48 h each film was removed

†The IUPAC name for glycidyl is 2,3-epoxypropionyl.

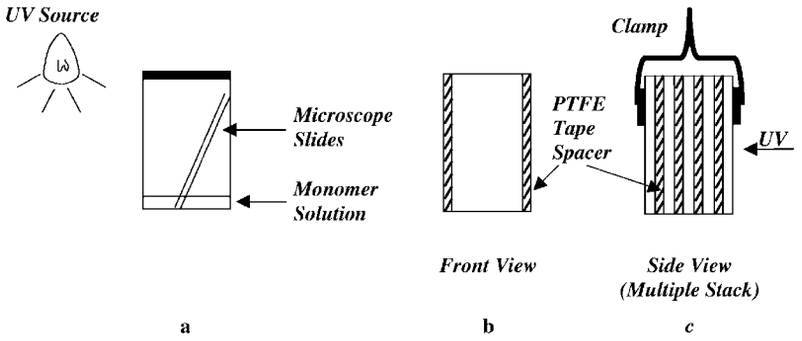


Fig. 1 a) Set up for the polymer film production; b) Placement of PTFE tape down the edge of the microscope slide as a spacer; c) Side view of the multiple assembly of the slides.

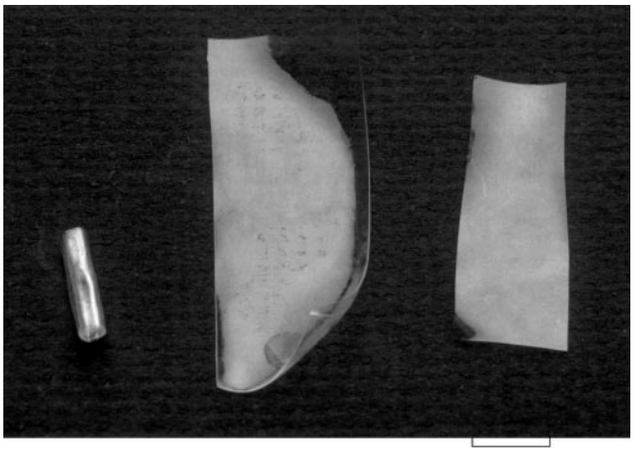
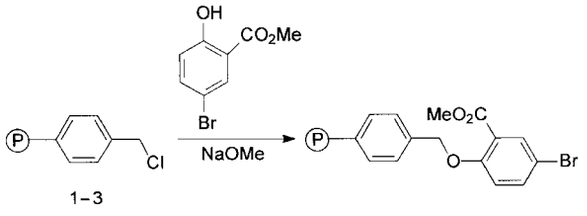


Fig. 2 Optical photograph of gel-type film **2**. Right: film after acetone extraction and vacuum drying; Left: dry film 'scrolled'; Centre: film swollen in xylene (Bar = 1 cm).



Scheme 1 Derivatising of gel-type VBC-containing films (**1**–**3**) with 5-bromosalicylic acid methyl ester in the presence of sodium methoxide.

from the reaction mixture with tweezers and washed by shaking consecutively in the solvents: THF, THF–H_2O (1 : 1), THF and MeOH and each was then extracted with acetone in a Soxhlet apparatus before vacuum drying. The analytical data in Table 2 confirm that chemical modification of the films has occurred. Again, however, species **1** proved difficult to handle without inducing mechanical damage.

The GMA-containing film **4** was also reacted with 2-aminomethylpyridine (Scheme 2) to assess the feasibility of exploiting the epoxide functionality. Elemental microanalytical data (C, 54.8; H, 6.2; N, 4.7%) indicated ~55% conversion of the theoretical epoxide group content.

Macroporous films

A range of macroporous styrene–DVB–4-vinylpyridine (4-Vpy) films were produced using a procedure similar to that used for the gel-type films. Table 3 shows details of some typical film formulations and characterisation data. Films recovered intact were extracted with acetone in a Soxhlet apparatus and vacuum dried. Toluene, xylene, *n*-butyl acetate, butan-2-one and hexane were also examined as potential porogens. The mechanical properties of the films produced were very porogen dependent. Toluene yielded films that were extremely soft in the swollen state and difficult to handle without damage. Xylene and *n*-butyl acetate yielded similar films that were difficult even to remove intact from the microscope slides. Hexane yielded highly opaque films which simply crumbled when attempts were made to isolate them. Likewise the films produced using dodecanol were of varying opacity and though these could be removed from the slides they were mechanically fragile and difficult to handle. The films produced employing 2-ethylhexan-1-ol were also of varying opacity but could be handled fairly readily without damage; likewise a few films produced using butan-2-one.

Dry films with a low level of 4-Vpy *e.g.* **5** and **9** were very white and obviously porous, while those with larger levels of 4-Vpy tended to be rather clear or only slightly opaque *e.g.* **8** and **12**. This visual difference was confirmed in the porosity data, notably surface area, determined from N_2 sorption isotherms using the BET equation.[14] Surface areas ranged from ~5–150 $m^2\ g^{-1}$ depending on the 4-Vpy content, and tend to parallel some surface area data of suspension polymerised resins prepared from similar polymerisation mixtures.[15] A scanning electron micrograph (JEOL JSM35; x750) (Fig. 3) of film **5** showed this to have a superficially smooth outer-surface (originally in contact with the glass slide) but a rugged porous morphology inside. The interconnectivity of the porous structure was demonstrated readily by dipping the base of a film in an acetone solution of Sudan red whereupon the dye readily migrated up the film much as in a thin layer chromatography experiment.

Table 1 Preparation of gel-type films[a]

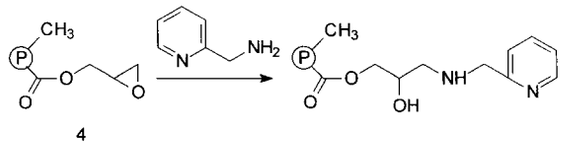
Entry	Monomer (g, mmol)	Functional Comonomer (g, mmol)	Crosslinker (g, mmol)	Initiator[b] (g)	Benzyl chloride content (mmol g^{-1})
1	Styrene (1.95, 18.7)	VBC (2.00, 13.1)	DVB (0.25, 1.5)	0.04	2.34
2	Styrene (1.00, 9.6)	VBC (1.00, 6.6)	PEG1000 DVBE[c] (1.00, 0.8)	0.04	2.25
3	Styrene (1.50, 14.4)	VBC (1.52, 10.0)	PEG1500 DVBE[d] (2.00, 1.2)	0.05	3.16
4	MMA (1.59, 15.9)	GMA (1.51, 10.6)	EGDMA (0.25, 1.3)	0.04	3.16[e]

[a]See Experimental section for details. [b]2,2′-Dimethoxy-2-phenylacetophenone. [c]PEG1000 DVBE = poly(ethylene glycol) α,ω-divinylbenzyl ether. [d]PEG1500 DVBE = poly(ethylene glycol) α,ω-divinylbenzyl ether. [e]Epoxide group content.

Table 2 Chemical modification of gel-type films[a]

Film	VBC / mmol	Mass of film /mg		Elemental microanalytical data (%)				Br in product /mmol	Conversion of CH_2Cl-groups (%)
		Before reaction	After reaction	C	H	Cl	Br		
1	0.28	87.5	107.4	71.8	5.5	3.1	7.4	0.100	36
2	0.16	69.6	89.9	68.6	6.3	2.0	5.8	0.063	40
3	0.19	81.5	104.2	69.1	6.5	0.6	8.5	0.110	58

[a]See Experimental section for details.



Scheme 2 Reaction of GMA-containing film **4** with 2-aminomethylpyridine.

Methylation of macroporous 4-Vpy films

As an example film **7** containing 1.0 mmol pyridine g^{-1} (22 wt% DVB–2-ethylhexan-1-ol porogen) was methylated using excess MeI in acetone. The film became markedly yellow (pyridinium iodide charge transfer absorption band) after 3 h refluxing. Microanalytical data for the acetone extracted and dried film (C, 77.3; H, 6.7; N, 1.2; I, 12.7%) suggests a pyridine content of $\sim$0.9 mmol g^{-1} and an iodide content of 1.0 mmol g^{-1} *i.e.* substantial methylation occurs readily. Ion exchange of the I^- by dipping into an aqueous $KMnO_4$ solution yielded a dark purple film, again confirming effective quaternisation. Treatment of a non-methylated sample of film by dipping into aqueous $CuSO_4$ solution yielded a pale blue film arising from coordination of pyridine groups to Cu(II).

Summary

A range of polymer supports of varying morphology can be prepared in a thin film format ($\sim$60–120 μm) by UV initiated polymerisation of appropriate comonomer mixtures sandwiched between microscope slides. Choice of copolymer composition allows respectably resilient films to be produced with reactive functionality present. The latter can be exploited in further chemical modification. While our own procedure yielded samples typically $\sim 76 \times 14$ mm in principle our approach and variants of it could be scaled-up to produce larger samples. In our hands it is possible to scroll-up suitable films (Fig. 2) and insert them for exploitation in teabags[16] or Irori microkans®.[17] With appropriate design they might also be scrolled and held on modified Chiron® pins.[7] While we do not envisage, or certainly not propose, that this thin film format has broad applicability, it has proved extremely useful in the hands of our collaborators for spectroscopic mechanistic studies; we believe that with the facile method of synthesis, others may also find it useful in similar studies and in trouble-shooting investigations.

Experimental section

Slide preparation

To prevent the polymer films produced adhering to the microscope slides the latter were first coated in silicone oil (2 wt% in methyl ethyl ketone) and baked in an oven at 200 °C for 18 h. After cooling the slides were wiped clean of any excess oil with tissue paper, before being stacked together in a multiple sandwich fashion with a PTFE tape acting as a spacer between each slide (Fig. 1). Up to 9 slides (8 films) were clamped together in the final assembly. The ends of the slides were left open to allow filling with comonomers by capillary action.

Preparation of films

All monomers employed were passed through a column of Al_2O_3 before use. Typically for **7** a mixture of styrene (18.6 g, 179 mmol), DVB (8.4 g, 80% grade, $\equiv$ 52 mmol $\equiv$ 22 wt% crosslinker), 4-vinylpyridine (3.15 g, 30 mmol) and 2,2′-dimethoxy-2-phenylacetophenone (0.3 g, 1 wt%) was prepared. This mixture (1.5 g) and an equal mass of porogen (when used) (*e.g.* 2-ethylhexan-2-ol for **7**) were then added to a glass bottle (500 ml) and the solution deoxygenated using a N_2 gas stream for 15–20 min. A microscope slide mould was then lowered into the solution, placed at a slight angle against the bottle side, and the bottle sealed with its cap. Polymerisation was induced by UV irradiation (BLAK-RAY Long wave UV-lamp Model B-100A or Model B-100AP, Upland, CA, USA) for 18 h. The films so formed were recovered by carefully delaminating the mould and gently peeling off the films from the slides if necessary with the aid of a razor blade. Each film was then washed by extraction with acetone in a Soxhlet apparatus for 3 h before drying under vacuum (40 °C).

Attachment of 5-bromosalicylic acid methyl ester to VBC-containing films 1–3

5-Bromosalicylic acid methyl ester (0.36 g, 1.6 mmol) and NaOMe (0.12 g, 1.6 mmol) were dissolved in dimethylacetamide (10 ml) under N_2. The film (**1**, **2** or **3**) was added and the reaction mixture heated to 90 °C with slow stirring for 48 h. The film was recovered with tweezers and washed by shaking

Table 3 Macroporous styrene–DVB–4-Vpy Films[a]

Film	Porogen[b]	4-Vpy[c] content /mmol g^{-1}	DVB (wt%)	Surface area /m^2 g^{-1}	Average pore radius /nm
5	2-Ethylhexan-1-ol	0.8	22	156	8.2
6	2-Ethylhexan-1-ol	0.9	22	117.0	7.4
7	2-Ethylhexan-1-ol	1.0	22	38.0	6.3
8	2-Ethylhexan-1-ol	1.8	11	5.0	1.2
9	Dodecanol	0.5	22	51.4	8.0
10	Dodecanol	0.7	22	46.6	4.8
11	Dodecanol	1.0	22	28.2	9.2
12	Dodecanol	1.6	22	22.1	3.4

[a]See Experimental section for details. [b]Mass equal to total mass of comonomers. [c]Calculated from N% analytical data.

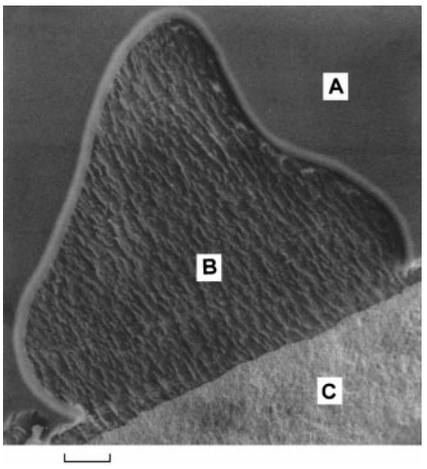


Fig. 3 Scanning electron micrograph ($\times 750$) of film **5**: A, superficially smooth surface originally in contact with glass; B, surface layer cleaved away to show rough interior; C, rough interior, edge view (Bar = 10 μm).

consecutively in the following solvents: THF, THF–H_2O (1 : 1), THF, and CH_3OH before extracting with acetone in a Soxhlet apparatus and vacuum drying (40 °C). Analytical data are shown in Table 2.

Amination of GMA-containing film, 4

The film, **4** (81.5 mg, 0.26 mmol epoxide) was placed in a solution of 2-aminomethylpyridine (0.49 g, 1.6 mmol) in dimethylacetamide (10 ml) and heated at 90 °C for 48 h. The film was recovered with tweezers and washed, extracted and dried as before.

Methylation of 4-vinylpyridine-containing film 7

Film **7** (1.0 mmol pyridine g^{-1}, 22 wt% DVB, 2-ethylhexan-2-ol porogen) was added to a solution of MeI (1.5 ml, 24 mmol) in acetone (10 ml). The mixture was refluxed for 3 h after which the film was yellow in colour. Excess reagent was removed by acetone extraction followed by vacuum drying.

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