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Fabrication of columns for open-tubular liquid chromatography using photopolymerization of acrylates

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ABSTRACT

In liquid chromatography, a significant improvement of separation can be achieved by using 5–10-μm I.D. open capillaries instead of packed columns. In these capillaries relatively thick (0.3–2 μm) films of stationary phases are required. These are difficult to prepare if polymer solutions are to be used. The fabrication of thick polymer films inside quartz-glass capillaries using chain cross-linking photopolymerization of monomers in liquid solution rather than cross-linking of polymers cast from solution is described. In a 9-μm capillary a film thickness of about 0.3 μm was readily prepared and plate numbers of $7 \cdot 10^4$ to $1.2 \cdot 10^5$ m^{-1} were obtained. The photopolymerization process can be carried out under either static or dynamic conditions. The latter method facilitates the manufacture of long columns with a length of several metres. The experimental conditions for making smooth coatings using a siloxane acrylate together with lauryl acrylate as a reactive diluent, and methods for inspection and testing of these columns, are described.

INTRODUCTION

Open-tubular liquid chromatography (OTLC) has the potential to become a useful method for very efficient separations of complex mixtures of thermally labile or non-volatile compounds. However, one of the major problems for the development of the technique is the necessity to combine a small inside diameter (I.D.) of the column with relatively thick stationary layers in order to combine a high efficiency with a sufficienct capacity for easy and accurate detection. Owing to the low diffusion rates

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of solutes in liquid mobile phases, the I.D. of the columns should be in the range 1–10 μm[1,2]. The use of such narrow columns implies very small peak volumes and, consequently, small injection and detection volumes. Therefore, special injection and detection devices have been developed. Nowadays it is possible to operate OTLC under optimum conditions, provided that suitable columns are available[3–9]. A particular drawback of small diameter columns is the difficulty of preparing suitable stationary phases with appropriate film thicknesses. In a 10-μm capillary the film thickness should be in the range 0.3–2 μm, depending on the diffusion coefficient of the solutes in the stationary phase[10,11].

Over the past few years considerable progress has been made in the preparation of stationary phases inside small I.D. capillaries[11–20]. Recently, a method was described for preparing a porous silica layer in 10-μm I.D. fused-silica capillaries[12–14]. The porous silica layer was prepared by coating the wall with poly(ethoxysilane) (PES), followed by conversion of PES into porous silica by treatment with ammonia. Columns prepared in this way showed good efficiency in liquid–liquid and reversed-phase chromatography. However, the phase ratios obtained by this procedure are insufficient as the thickness of the PES film is restricted by the coating procedures (the phase ratio is defined as the accessible surface area of the stationary phase divided by the volume of the mobile phase).

Apart from the preparation of porous layers, most progress has been made with the fabrication of columns coated with polysiloxanes using either static[11,12,17–19] or precipitation coating[20]. Very efficient columns have been prepared from 5- and 10-μm I.D. capillaries. However, just as with the porous silica layers, static evaporation coating procedures yielded only thin films, especially in the 5-μm I.D. capillaries. So far it has proved impossible to prepare films thicker than about 0.03 μm. The limitation of the thickness is caused by several factors. First, a very high concentration of polymer would be required. Second, the polymer solution should have a high viscosity in order to form a uniform and smooth film but Rayleigh instability should be avoided[21]. However, it is very difficult to filtrate concentrated, viscous solutions and to fill capillaries with them. Finally, the evaporation of the solvent from such solutions contained in a narrow capillary becomes prohibitively slow.

The precipitation coating procedure as introduced by Dluzneski and Jorgenson[20] has yielded thick films of polysiloxane phases. This procedure is very elegant and it has been demonstrated that coatings with suitable thicknesses in 5-μm I.D. columns with lengths of up to 3 m can be obtained in a relatively short time.

As an alternative to the techniques mentioned above, it was attempted to prepare thick stationary phases using *in situ* photopolymerization of a solution of a monomer and a photoinitiator, followed by evaporation of the solvent from the polymeric gel. This approach offers several advantages over the above-mentioned procedures:

(i) Low-viscosity monomers can be used to facilitate the filling of the narrow-bore capillary. A low viscosity also allows easy filtration of these monomers, which will prevent blockage of the column by impurities such as dust particles.

(ii) A wide choice of monomers is available. Within the class of highly reactive acrylates, for example, the polarities cover a wide range. This allows the manufacture of columns with, in principle, widely differing separation properties.

(iii) The polymer layers will have a higher stability if they are chemically bonded to the surface of a column. The surface of a column can be easily modified by silylation

with a compound containing acrylate groups. Copolymerization with the monomer then provides permanent adhesion.

The principles and use of photopolymerization in various manufacturing processes have been described, together with the relationship between monomer structure and some polymer properties[22].

This paper describes the preparation of a 0.5–1.0-μm thick polymer film inside 5–80-μm I.D. quartz-glass capillaries by means of *in situ* photopolymerization in solution using a siloxane acrylate as a cross-linking oligomer together with lauryl acrylate as a reactive diluent. The chromatographic properties of columns made in this way are described.

EXPERIMENTAL

Materials

Silica capillaries of 9–80 μm I.D. were made at Philips Research Laboratories in a similar way to optical fibres for telecommunication[23], but using a silica tube instead of a massive preform. Their outsides were coated with UV-cured acrylate polymers as are used for optical fibres (DS042 from DeSoto, DesPlaines, IL, U.S.A.). Commercially available capillaries, coated with a film of UV-absorbing polyimide, proved inadequate for *in situ* photopolymerization. Silica glass plates of 30–40-mm diameter were used as test disks for surface treatments.

Toluene (Merck, Darmstadt, F.R.G.) was dried over molecular sieves 4 A (Janssen, Beerse, Belgium). Chloroform, 2-propanol, tetrahydrofuran (THF), pentane and hexane (analytical-reagent grade, Merck) were used as supplied. Methanol (Merck) was used as a mobile phase for chromatographic testing. 3-(Methacryloxy)propyltrimethoxysilane (γ-MPS) (Petrarch Systems, Bristol, PA, U.S.A.) was distilled under reduced pressure. 3-(Acryloxy)propyltrimethoxysilane (γ-APS) (Petrarch Systems) and *n*-octyltriethoxysilane (n-OS) (Petrarch Systems) were used as supplied. Tetraethylene glycol diacrylate (TEGDA) (Polysciences, Warrington, PA, U.S.A.) and lauryl acrylate (LA) (Polysciences) were used without distillation. In addition to these monomers, a silicone acrylate (SiA; RC 710) (Goldschmidt, Essen, F.R.G.) was used. This acrylated dimethylsiloxane oligomer has a viscosity of 200 mPa s. Determination of unsaturation (by bromine addition) yielded a double bond content of 2.23 mmol g^{-1}, which corresponds to an acrylate equivalent weight of 450 g. α,α-Dimethoxy-α-phenylacetophenone (DMPA; Irgacure 651) (Ciba-Geigy, Basle, Switzerland) was used as a photoinitiator. Various anthracene derivatives were used as model compounds for testing the chromatographic properties.

Internal silylation of capillaries

Filling and washing of long capillaries (length 2–5 m, I.D. 80, 65, 10 and 9 μm) with solutions was carried out using a small reservoir pressurized with helium[14]. Silica capillaries were drawn at a temperature of 2000°C, which resulted in a very low density of surface silanol groups (SiOH). As in the silylation reaction the silane reacts with a silanol group, but not with a siloxane group, some of the siloxane groups must be converted into silanol groups. Therefore, the inner surfaces of the capillaries were etched with an alkaline solution using the method reported by Tock *et al.*[14]. A 1 *M* solution of potassium hydroxide was pumped through a silica capillary at room

temperature for about 2 h, using the pressurized vessel. After etching, the capillary was washed, first with water, then with 0.03 *M* hydrochloric acid for about 2 h, and finally with water until the effluent was neutral. Next, the capillary was dried at 125°C under a stream of helium for at least 4 h. The silylation was carried out by pumping a solution of silane in toluene (1–2%, v/v) through the etched capillary at 125°C for 1 h. The capillary was placed in an oven to control the temperature. Subsequently, it was washed with toluene and dried at room temperature under a stream of helium for at least 3 h.

Formation of polymer films inside capillaries

Two different means of UV irradiation were adopted, depending on the length of the capillaries. With test capillaries shorter than 60 cm UV irradiation was carried out statically, using one lamp (Philips, TLD 18W/08, length 60 cm). With capillaries longer than 60 cm dynamic irradiation was carried out by moving the capillary at a constant rate along the light source and using a longer lamp (Philips, TLD 36W/08, length 120 cm). This method is suitable for the preparation of columns of appreciable length. The light intensity distribution along the length of these long lamps was carefully checked with an International Light IL 745a UV-curing radiometer before use. After irradiation, the solvent was evaporated from one end of the capillary in a vacuum oven (pressure 15–20 kPa). The column was kept in the oven for at least 15 h. In view of the proposed mechanism of film formation (see below), it is obvious that the process has to be performed very carefully. Boiling of the solvent should be prevented at any time as this would promote irregular rupture of the gel. Finally, the capillary coating was thermally cured at 120°C, during at least one night.

Measurement of contact angles

In order to check whether surface treatments were effective or not, the wetting of the surface by a test liquid was observed before and after treatment[24]. On flat disks the contact angle θ between a sessile droplet of 3 μl and the surface was measured using a Raine–Hart goniometer. In capillaries the contact angles were obtained by measuring the rise of a test liquid inside the capillary. The filled capillary was left intact for at least 20 h until a constant reading of the rise of the test liquid was attained. Water was mainly used as a test liquid.

Chromatography

The chromatographic properties of 9-μm I.D. internally coatad capillaries were measured using the system for OTLC, shown in Fig. 1[14]. It consists of a thermostated solvent reservoir (volume 400 ml) which can be pressurized with helium, and serves as a constant-pressure pump. A 0.5-μl injection valve (Model 7520; Rheodyne, Berkeley, CA, U.S.A.) equipped with a splitting device is installed between the pump and the capillary column. A helium–cadmium laser (Model 356 XM; Omnichrome, Chino, CA, U.S.A.) is used as the light source for on-column fluorescence detection. The laser beam passes a 325-nm bandpass filter (Oriel, Stratford, CT, U.S.A.) and is focused with a quartz-glass lens (f = 50 mm) at the end of the capillary. The external protective coating of the capillary must be burned off at the end of the column over a length of 1 cm. The emitted light is collected at an angle of 90° by a Fresnel lens (f = 16 mm), then passes a 380-nm cut-off filter (Oriel). The intensity is measured with a photo-

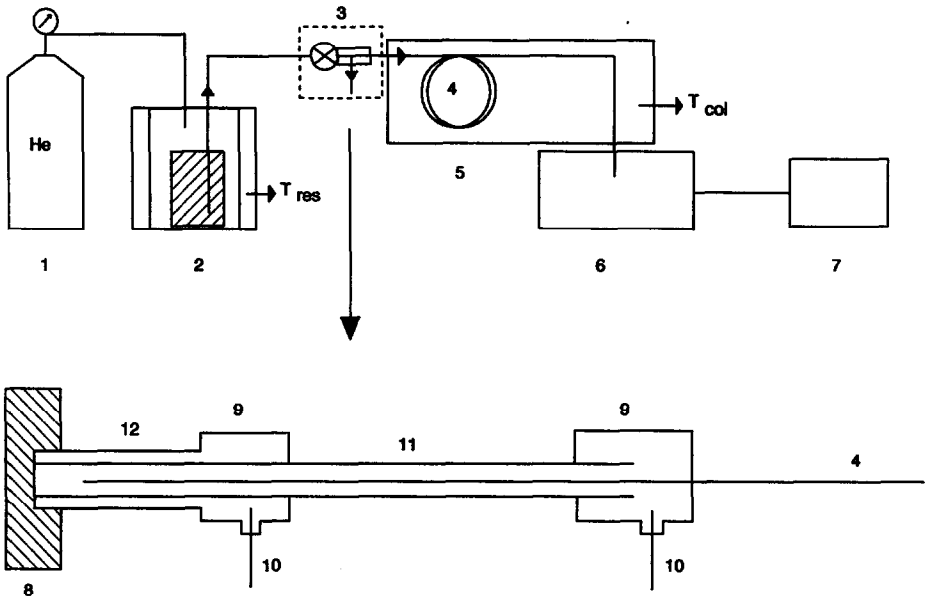

Fig. 1. Chromatographic set-up. 1 = Helium bomb; 2 = thermostated solvent reservoir; 3 = injector provided with a dual splitting device; 4 = capillary column; 5 = thermostated jacket; 6 = laser-induced fluorescence detector; 7 = strip-chart recorder; 8 = injector; 9 = 1/16-in. Swagelok union tee; 10 = waste capillary; 11 = fused-silica capillary, I.D = 300 μm; 12 = 1/16-in. stainless-steel tubing.

multiplier tube (Type 625 S; EMI, Hayes, U.K.). The photocurrent is amplified and converted into a voltage by means of an amplifier (Diomod 72-W; Knick, Berlin, F.R.G.). The signal is recorded with a potentiometric recorder (Siemens, Karlsruhe, F.R.G).

Methanol was used as the mobile phase throughout this study.

RESULTS AND DISCUSSION

Surface treatment of capillaries

In order to ensure proper adhesion of the polymer film to the wall of the capillary, the surface has to be reacted with a silane coupling agent possessing a copolymerizable (meth)acrylate group such as γ-MPS.

Treated capillaries were tested by determining contact angles from the capillary rise. Capillary rise measurements with water required a length of at least 50 cm in the case of a 80-μm I.D. capillary. Table I shows the change in contact angles in 80-μm I.D. capillaries observed after various surface treatments. Silylation causes a considerable increase in the contact angle. As in control experiments using flat disks even higher values were obtained, it was assumed that the capillary surface has a lower surface concentration of reactive SiOH groups than that of the disk. In order to achieve a maximum surface coverage, the capillaries were etched with dilute alkali solution. Etching reduces the contact angle of both capillaries and disks and subsequent silylation increases it again. The effect of etching on the ultimate contact angle is largest with the capillaries.

TABLE I

EFFECT OF VARIOUS SURFACE TREATMENTS ON CONTACT ANGLES OF WATER AT 20°C

No.	*Etching*	*Silylation (γ-MPS)*		*Contact angle, θ (°)*	
		Temperature (°C)	*Time (min)*	*Capillaries*	*Flat disks*
1	No	–	–	35–38	43
2	No	120	60	62	66
3	Yes	–	–	9	<5
4	Yes	120	60	74–82	67

Formation of polymer films inside silylated capillaries

Silicone resins have often been selected as stationary phases, as they show a very restricted swelling in polar solvents and as high diffusion coefficients of solutes have been reported[11,18,19]. A silicone acrylate resin (SiA) having the lowest viscosity available (0.2 Pa s) was selected. The silicone acrylate resin is basically a dimethylsiloxane, modified by substitution of acrylate groups. Polymer films could be obtained inside capillaries with an I.D. of 65 μm. However, filling with methanol not only caused a strong swelling of the gel but even complete blocking of the capillary occurred. A possible explanation of this unexpected behaviour is irregular rupture of the network, caused by too strong or inhomogeneous cross-linking[22] or by insufficient control of the rate of solvent evaporation. In order to obtain a more uniform polymer film, the cross-link density was reduced by the addition of LA [SiA/LA = 1:1 (w/w)]. The photoinitiator content was 2% (w/w) with respect to total monomer.

This mixture was applied to capillaries with a length of 1 m. The dynamic irradiation procedure was used in order to eliminate the effect of intensity variation along the fluorescent lamp. The capillaries were irradiated at a light intensity of 0.35 mW cm^{-2} and moved at a constant rate of 1.9–2.0 mm s^{-1}, so that the exposure time was 5 min. Next, THF was evaporated from one end of the capillary at 30°C under reduced pressure (15–20 kPa). Photographs of the cross-section and the outside of a capillary are shown in Fig. 2. In all sections almost the same cylindrical shape of the polymer film was observed. Next, the swelling behaviour of the polymer films was investigated in order to check whether blockage takes place inside the capillary. Fig. 3 shows a photograph of a polymer film after filling the capillary with methanol. From Figs. 2 and 3 it can be seen that there was no significant swelling of the polymer films, as could be expected from the large difference in solubility parameters of the polymer and methanol, respectively. Further, it has been reported that the degree of swelling of pure polydimethylsiloxane by methanol is very small[18]. The present polymer film appears to withstand methanol and other polar solvents, which prevents blockage of the capillary by swelling.

Finally, similar polymer films were made inside narrow-bore capillaries using the same procedure, except that the evaporation of THF was carried out at 60°C. In Fig. 4 scanning electron micrograph of a polymer film inside a 9-μm I.D. capillary (length 80 cm) is shown. The thickness of the film was estimated to be 0.3–0.4 μm. The uniformity of the film could not be assessed by microscopy.

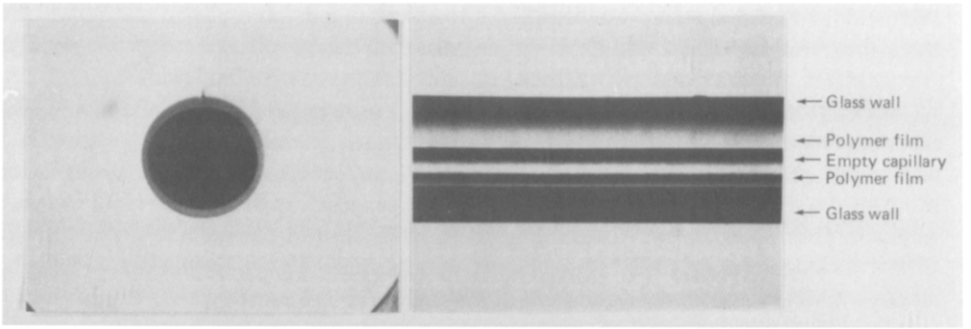

Fig. 2. Cross-section and side view of internally coated capillary with I.D. 65 μm and length 1 m. Viewed on its side, the bore of the capillary looks narrower than it is. This is due to refraction. Monomer: SiA–LA (1:1) with 2% (w/w) DMPA in THF. Monomer concentration: 30% (w/w). UV intensity: 0.35 mW cm^{-2}. Exposure time: 5 min.

The formation of cylindrical films is not always observed. When, for example, TEGDA was used as a monomer, with DMPA as the photoinitiator and THF as the solvent, a peculiar film shape was obtained (Fig. 5). The same characteristic "eye" shape was observed in a narrow-bore (9-μm I.D.) capillary. With increasing monomer concentration thicker films were formed but the "eye" shape of the film also became more prominent (Fig. 5b). At even higher concentrations films with a rough surface and numerous small plugs were formed. The typical "eye" shape is probably caused by rupture of the cylindrical gel on evaporation of the solvent. During polymerization in solution a strongly swollen gel is formed. On evaporation of the solvent the gel will tend to reduce its volume. As the gel is bonded to the wall, it can do so only by delamination or by rupture. Controlled rupture requires the control of cross-link density. Reduction of the cross-link density of the polymer network by adding a monoacrylate such as LA gave some improvement of the shape and the regularity of the polymer film but films of such compositions were unsuitable for chromatography

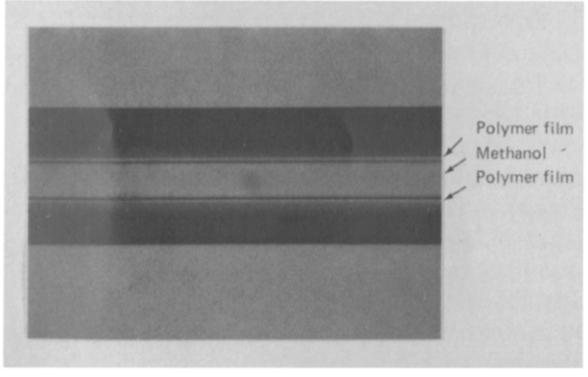

Fig. 3. Side view of a SiA–LA polymer film in a capillary with I.D. 65 μm after filling it with methanol. Preparation as in Fig. 2.

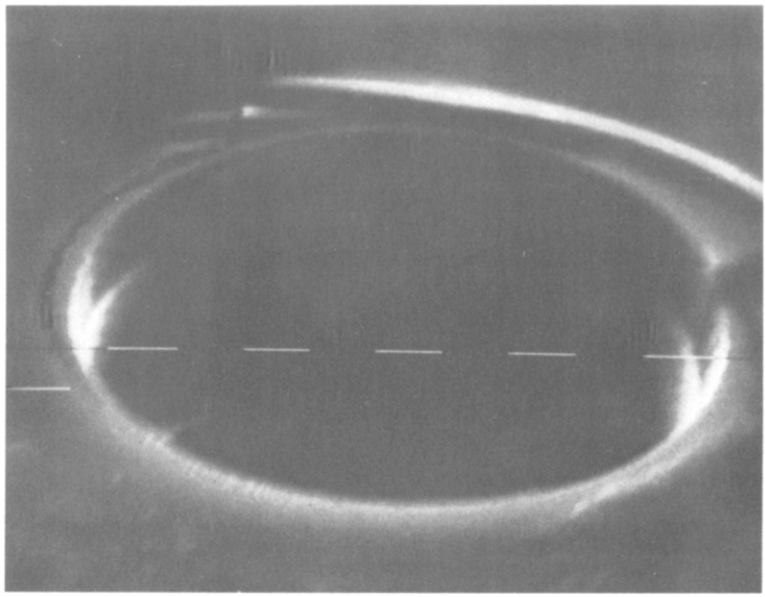

Fig. 4. Scanning electron micrograph of a polymer film inside a capillary with I.D. 9 μm. The film is just visible near the second and sixth white markers. Marker length, 1 μm. Preparation as in Fig. 2.

as swelling by the methanol eluent caused complete blocking of the column. Therefore, only the SiA–LA mixture was further investigated.

The proposed mechanism of film formation is further amplified by the observation that in capillaries which were treated with a non-copolymerizable silane such as n-OS a filament was formed instead of a film. This also emphasizes the necessity to use a coreactive silane coupling agent.

Chromatography

Fig. 6 shows a chromatogram of the separation of eight polycyclic aromatic hydrocarbons (PAHs) in an 8.5-μm I.D. capillary coated with the SiA–LA polymer, described above. Photopolymerization reduced the I.D. to 7.7 μm, as measured by the methods reported by Tock *et al.*[14]. The eight PAHs were well separated using pure methanol as the eluent. For 9-hydroxymethylanthracene and 9,10-diphenylanthracene capacity factors (k') of 0.18 and 2.05, respectively, were obtained. Compared with the separation on a conventional reversed-phase packing of C_{18}-modified silica particles in a packed column, using pure methanol as the eluent, the separation on the polyacrylate-coated capillary column is good. The column is very hydrophobic owing to the presence of the lauryl chains in the polymer and therefore the PAHs elute only with a solvent with a high eluting strength.

In Fig. 7 an H *vs.* u curve is shown for the PAHs. It can be seen that the measured plate height, H, of the solutes increases linearly with the linear velocity, u. The diffusion coefficients of the solutes in the stationary phase (D_s) were calculated from the slope of these lines by subtracting the calculated mobile phase diffusion (C_m) term.

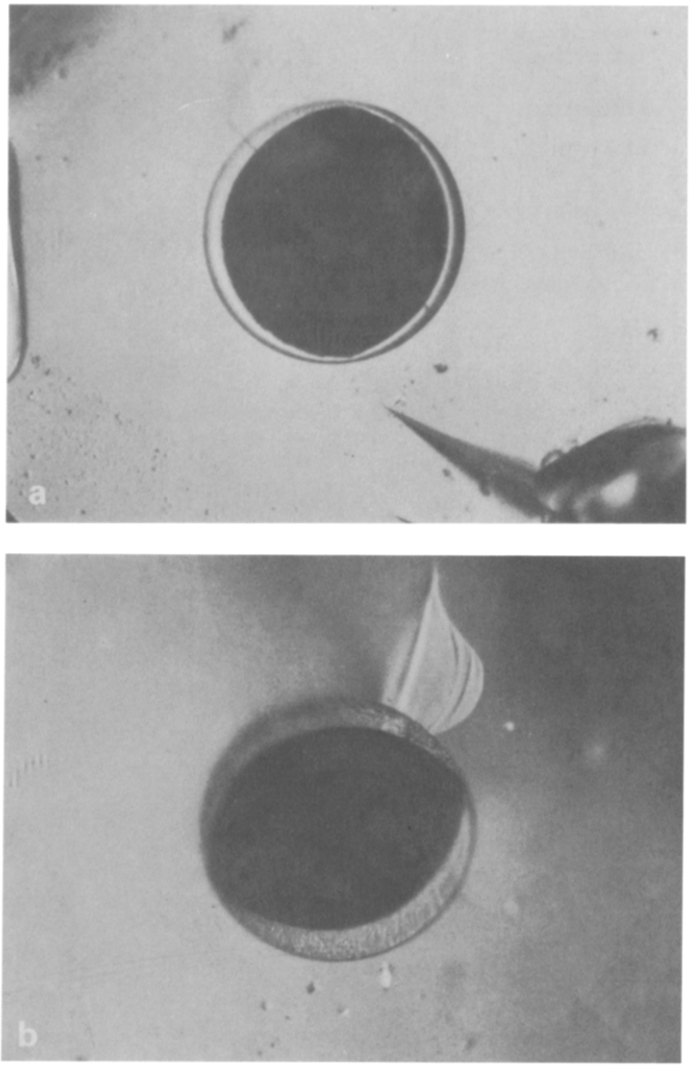

Fig. 5. Cross-section of internally coated capillaries with I.D. 65 μm. Monomer: TEGDA with 4% (w/w) DMPA in THF. Monomer concentration: (a) 20; (b) 30% (w/w). UV intensity: 0.52 mW cm^{-2}. Exposure time: 5 min.

In this calculation the value of the solute diffusion coefficient in the mobile phase (D_m) was taken to be 10^{-9} m^2 s^{-1}; k' and I.D. were determined experimentally. It was further assumed that no additional band broadening is introduced by irregularities of the film. The D_s values were found to be in the range $5 \cdot 10^{-12}$–$2 \cdot 10^{-11}$ m^2 s^{-1}; for anthracene $D_s = 2 \cdot 10^{-11}$ m^2 s^{-1}. If we compare this value with the reported value of $6 \cdot 10^{-12}$ m^2 s^{-1} for anthracene in a cross-linked silicone phase OV-101[11] it can be concluded that the present column material can be used at large thicknesses. Columns

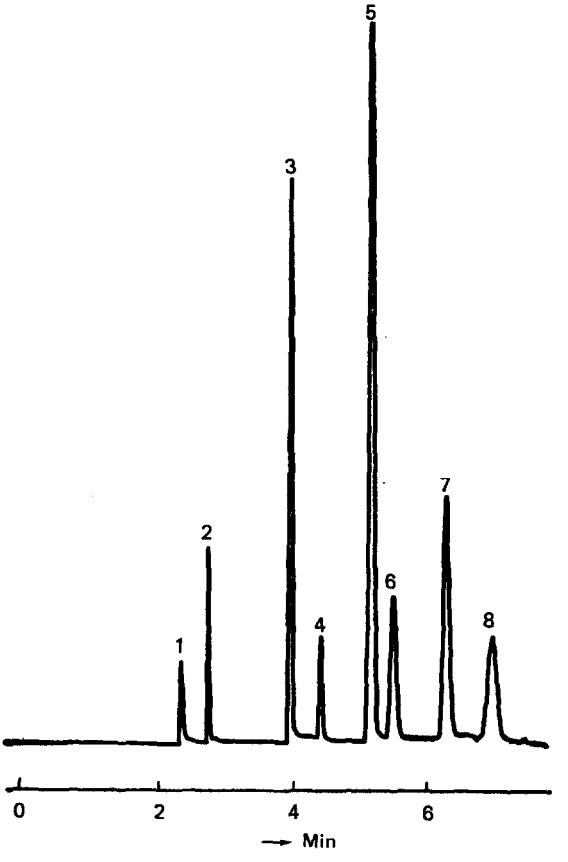

Fig. 6. Chromatogram obtained with the column shown in Fig. 4. Column dimensions: I.D. 7.7 μm, length 0.75 m. Mobile phase: methanol. Film thickness: 0.39 μm. Injection volume: 15 pl. Linear velocity: 5.5 mm s^{-1}. Pressure drop: 1.5 MPa. Solutes: 1 = fluorescein; 2 = 9-hydroxymethylanthracene; 3 = 9-cyano-anthracene; 4 = anthracene; 5 = fluoranthene; 6 = 9-phenylanthracene; 7 = 1,2-benzanthracene; 8 = 9,10-diphenylanthracene.

coated with layers 0.3–0.4 μm thick will support a considerably higher loading than the cross-linked OV-101 phase. Consequently, fewer detection problems are expected. As the D_s values of the solutes in the acrylate polymer are not known, it is not possible to compare the performance of the present column with theoretical plate-height estimates. To do so, it would be necessary to measure the diffusion coefficients of the solutes in the polymeric material used.

In Fig. 7 it can be seen that the efficiency obtained for anthracene is better than that for 9-hydroxymethylanthracene, although the k' value of the latter is smaller. The same observation was made with benzanthracene and phenylanthracene. This effect is not yet understood, it could perhaps be due to differences between the D_s values of the two pairs of solutes.

From the data shown in Fig. 7, plate numbers can also be calculated. These were found to be of the order of 10^5 m^{-1} for $u \approx 0.6$ mm s^{-1} and of the order of 10^4 m^{-1} for the highest linear velocities.

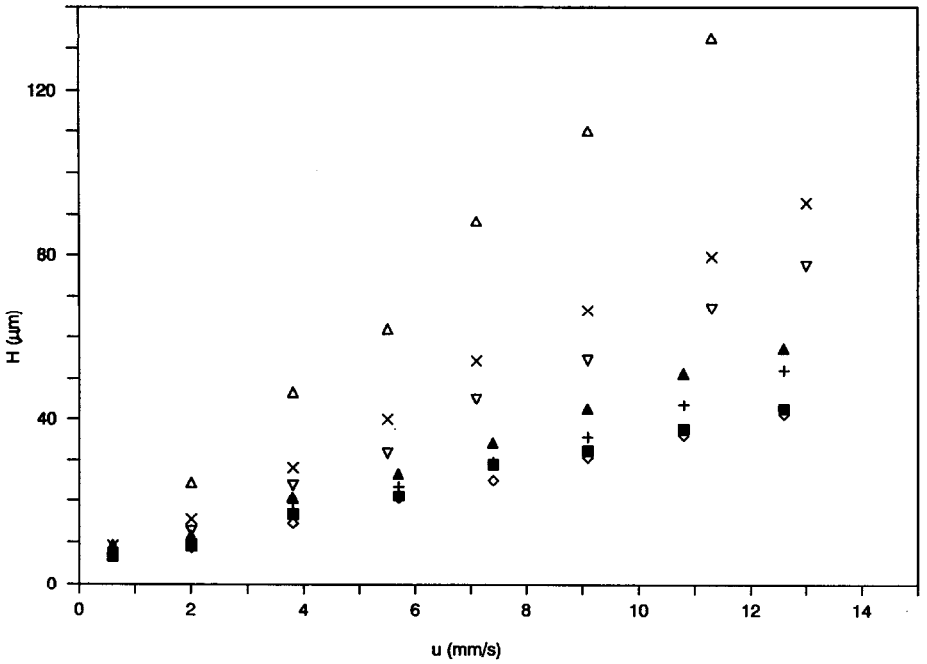

Fig. 7. Plate height H *vs.* linear velocity u for the column, eluent and solutes used in Fig. 6. Solutes ■ = 9-hydroxymethylanthracene, $k' = 0.18$; + = 9-cyanoanthracene, $k' = 0.71$; ◇ = anthracene, $k' = 0.91$; ▲ = fluoranthene, $k' = 1.25$; × = 9-phenylanthracene, $k' = 1.4$; ▽ = 1,2-benzanthracene, $k' = 1.75$; △ = 9,10-diphenylanthracene, $k' = 2.05$.

The performances of two other 8-μm I.D. columns, prepared in the same way as described above, were similar to that of the column described.

CONCLUSIONS

In situ photopolymerization of acrylic monomers in a 9-μm I.D. capillary has yielded a stable retentive layer with a suitable film thickness of about 0.4 μm. The chromatographic performance of the columns obtained sofar is very good, although a final evaluation would require a knowledge of the diffusion coefficients of test solutes in the acrylate photopolymer.

Filling of narrow-bore capillaries with a length of several metres with concentrated, dust-free solutions of monomers (as required for the formation of thick and smooth films) turned out to be easy.

Another feature of the reported method is that one can make columns of widely differing polarities, simply by changing the monomer. The swelling behaviour of the polymeric network can be controlled by variation of the cross-link density through the addition of non-cross-linking monomers.

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