

## HYBRID SILICA POLYMER SORBENTS FOR HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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The obtaining of hybrid mineral polymer sorbents, based on wide-porous microspherical silica gels and polymer components, has been discussed. The possibility to apply the obtained sorbents in reversed-phase high performance liquid chromatography has been confirmed. Introducing the polymer layer onto the surface of microspherical silica gel has been realized by means of “dry polymerization” of corresponding monomers in the adsorbed layer of the porous matrix surface.

**Keywords:** mineral polymer packings, reversed-phase high performance liquid chromatography, poly-octadecylmetacrylate (Poly-ODMA), poly-octadecylmethacrylate-methylmethacrylate (Poly-ODMA-MMA), poly-octadecylmethacrylate-methylmethacrylate-divinylbenzene (Poly-ODMA-MMA-DVB), dry polymerization.

**Introduction.** The development of new methods for synthesis of packing materials for chromatography aiming to improve their structure and chromatographic parameters always was and remains significant even today. Most often, researchers turn to different means of modification of the surface of already existing chromatographic systems. Reversed phase high performance liquid chromatography (RP-HPLC) is considered as the most popular HPLC technique. At present silica remains the most widely used packing material for HPLC [1–4].

The modification of porous silica by organic compounds with different functional groups occupy the central place during the design of HPLC packings [5].

Silanol groups play a key role during the modifying process of the silica gel surface by series of modifiers (in particular, alkylchlorosilanes) [6]. The presence of silanol groups grafted to the surface of the obtained phases is mandatory. At the same time, this fact causes problems during chromatography of basic natural compounds (peaks “tailing”, restricted pH-stability range, etc.) [7–8]. Different methods are used to avoid these disadvantages of the silica gel packings. In our opinion, among these methods the polymer modification (more exactly encapsulation of the silica surface) may be the most reliable.

The polymer based chromatographic materials possess some disadvantages: they do not have hard structure, are less efficient, swell in the organic solvents [3]. The joining of positive properties of these components permits to obtain hybrid

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mineral polymer (silica-polymer) packings deprived of disadvantages intrinsic to silica and polymer materials.

The polymer modification of porous systems (particularly, silica gel) surface has series of advantages in comparison with alkylsilanes:

- The disadvantages of silica materials are eliminated.
- The quantity of the inserted phase is not restricted.
- It is possible to introduce simultaneously several functional groups (including the groups with inverse polarity).
- Such systems may be successfully applied in RP-HPLC [9–12].

**Experimental Part.** Micro-spherical silica gel (MSG) with the following characteristics has been used as the initial porous silica: specific surface area  $S_{sp} = 80 \text{ m}^2/\text{g}$  specific pore volume  $V_{sp} = 0.50; 0.57; 0.70 \text{ cm}^3/\text{g}$ , average pore diameter  $d_{av} = 30 \text{ nm}$ , particle size  $d_p = 7.5 \text{ }\mu\text{m}$ , obtained by hydrothermal treatment ( $T = 200^\circ\text{C}$ : duration – 4 h, pH 8.0). The process was carried out in the 0.5 L capacity autoclave: solid : liquid ratio = 1 : 14, autoclave loading level 0.8. Poly-octadecylmetacrylate (poly-ODMA), poly-octadecylmethacrylate-methylmethacrylate (poly-ODMA-MMA), poly-octadecylmethacrylate-methylmethacrylate-divinylbenzene (poly-ODMA-MMA-DVB) co-polymers have been used to coat silica gel surface.

Monomers and initiator of the polymerization – dicumyl peroxide (DCP), were obtained from “Aldrich”. The polymer component content was determined gravimetrically (after baking at  $800^\circ\text{C}$  during 4 h).

№	The initial monomer content (% of the total mass)			Column	Total polymer content	ODMA-groups content	C <sub>18</sub> -groups content	Phenyl-groups content from DVP	Peak retention time, min		<i>k'</i>
	ODMA	MMA	DVB						Uracil	Toluene	
1	100	–	–	ODMA-15	15.0	15.00	11.25	–	1.47	5.07	2.44
2	50	50	–	ODMA-MMA	20.0	10.00	7.50	–	1.76	3.46	0.97
3	50	50	–	ODMA-MMA	27.3	13.35	10.24	–	1.36	4.60	2.29
4	50	50	–	ODMA-MMA	33.3	16.67	12.50	–	1.32	6.10	3.63
5	42	42	16	ODMA-MMA-DVB <sup>a</sup>	25.0	10.50	7.88	4.0	1.56	8.14	4.21
6	42	42	16	ODMA-MMA-DVB <sup>b</sup>	25.0	10.50	7.88	4.0	1.62	8.50	4.25
7	42	42	16	ODMA-MMA-DVB <sup>c</sup>	25.0	10.50	7.88	4.0	1.73	9.20	4.32

Note: <sup>a</sup> –  $V_{sp} = 0.50 \text{ cm}^3/\text{g}$ ; <sup>b</sup> –  $V_{sp} = 0.57 \text{ cm}^3/\text{g}$ ; <sup>c</sup> –  $V_{sp} = 0.70 \text{ cm}^3/\text{g}$ .

Silica beads were added to the solution of monomer and DCP in *n*-pentane. The monomers composition and their quantities are given in the Table. DCP quantity consists 5.0 mass.% of the total monomer mass. Subsequently, the evaporation of the solvent was carried out in a rotary evaporator. Temperature was initially increased to 100°C over 1 *h* and kept at this temperature for an hour, then heated to 130°C over 1 *h* and kept at this temperature for an hour. The sorbent thus obtained was rinsed with a hot mixture of dimethylformamide-toluene, further with ethanol then dried by acetone on a filter. The final drying of the samples was carried out in the drying oven at 120°C during 2 *h*. Chromatographic investigations have been carried out on Waters HPLC system (Waters 626 Pump, Waters 600 Controller, Waters 486 Tunable Absorbance Detector) using 150×4.6 *mm* columns. An acetonitrile-water (50/50) mixture was used as a mobile phase (pH 7.0; flow rate 1 *mL/min*). Absorbance was measured at UV 254 *nm* wavelength.

**Results and Discussion.** The chromatographic data for separation of uracil/pyridine/phenol/toluene test mixture (are presented in Table, line 1) was obtained with the column packed by MSG modified by ODMA homopolymer. The toluene retention time in the given case is 5.04 *min*, which is 1 *min* more than its retention time on the Si-300 C<sub>18</sub> column. It is notable that ODMA homopolymer practically screens the silanol groups on the silica gel surface, which is proved by coincidence of the retention times for pyridine and phenol.

Apparently the “methacrylate” part of the polymer “secures” the polymer encapsulation of the surface and the “octadecyl” part – provides the presence of the C<sub>18</sub>-groups on it. 15.0 mass.% polymer content on the surface provides about 10.0–12.0 mass.% C<sub>18</sub>-groups content, which exceeds two times the amount of the reversed phase obtained as a result of modification of the surface by octadecyltrichlorosilane ODS [13]. The increase of the toluene retention time from 3.70 to 5.04 *min* may be explained namely by this circumstance.

The increase of the toluene retention time depends on the increase of the polymer (ODMA-MMA) quantity introduced onto the silica gel surface. Conceivably, structuring of the polymer occurs and the influence of this phenomenon becomes more appreciable with the increase of polymer quantity. Such assumption is based on the fact that the reverse picture must be observed with the increase of polymer quantity.

Namely, the retention time for the toluene must decrease as much as the surface area value of the porous material decreases when polymer content increases. This fact contradicts the known equation connecting the retention factor with the specific surface area values:

$$k' = S/V_m K,$$

where *S* is the surface area of the column, *V<sub>m</sub>* is the volume of the mobile phase in the column, *K* is the distribution coefficient.

One can solve this problem only assuming that the polymer introduced into the surface possesses its own porosity. Only in this case it becomes possible to involve more C<sub>18</sub>-groups onto the chromatography process. The introduction of DVB to the co-polymer composition increases the porosity of the obtained polymer coat (see Table, lines 5–7). This allows involving of higher number of phenyl and C<sub>18</sub>-groups into the chromatographic process. The accessibility of the surface for modification by silanes is determined by porous characteristics of the sorbent. In

case of polymer modification the situation looks a bit different. As the value of the specific surface area isn't the limiting factor for the quantity of the modifier (most likely pore volume, and average pore diameter in some level) then in this case polymer coatings consisting of several layers may be obtained. In addition, mutual overlapping of functional groups takes place when increasing the quantity of the polymer introduced. Furthermore, as a result of the polymer layer structuring, it is not only the maximal participation of the whole amount of the C<sub>18</sub>-groups that influences the toluene retention time. It is necessary to account the influence of phenyl groups of the DVB as well, because it is known that such groups are not inferior to C<sub>18</sub>-groups by their hydrophobicity.

It is evident that the modification by the ODMA homopolymer in 15.0 mass.% quantity secures 11.5 mass.% C<sub>18</sub>-groups content and the toluene retention time is 5.04 *min*. When modifying by ODMA-MMA copolymer, the toluene retention time increases with the increase of the introduced polymer quantity. When the polymer content is 33.33 mass.%, ODMA content equals to 16.67 mass.%, which corresponds to the 12.5 mass.% C<sub>18</sub>-groups content. The toluene retention time in this case is 6.10 *min*.

One can see from the dependence of the toluene retention time on the C<sub>18</sub>-groups content for the ODMA-MMA systems, that the retention time values are somewhat higher as compared with ODMA homopolymer. It is necessary to note that in the latter case the pore volume is lower than in the first case owing the presence of the MMA in the polymer composition.

According to the toluene retention time 5.50 *min* corresponds to the 11.25 mass.% C<sub>18</sub>-groups content. Actually it equals to 5.07 *min*. One can thus conclude that the polymer layer is more structured (more porous) in the ODMA-MMA system. We assume that some part of the C<sub>18</sub>-groups in the pore spaces is inaccessible for chromatography process. The chromatograms of the systems modified by ODMA-MMA-DVB copolymer prove this fact. When the total content of phenyl and C<sub>18</sub>-groups does not exceed 11.88 mass.% (12.0 mass.%) the calculated value of the toluene retention time must be 5.70 *min*, while actually it is equal to 8.14–9.20 *min*, which is one and a half times higher than for systems without DVB. The last three lines of the Table correspond to the hybrid sorbent samples obtained on the base of silica gels with specific pore volume  $V_{sp} = 0.50; 0.57; 0.70 \text{ cm}^3/\text{g}$  correspondingly. When pore volume increases from 0.50 to 0.70  $\text{cm}^3/\text{g}$ , the toluene retention time increases from 8.14 to 9.20 *min*.

So, it is more expedient to use silica gels with comparatively higher pore volume to prepare polymer containing sorbents as the hybrid silicapolymer sorbents, obtained according to the elaborate technique possess higher capacity.

**Conclusion.** The polymers introduced onto the silica surface possess their own porosity. The porosity of the polymer layer increases in poly-ODMA, poly-ODMA-MMA, poly-ODMA-MMA-DVB series. The increase of toluene retention time is observed when polymer layer composition is multicomponent and the sewing agent (DVB) is introduced. This may be explained by the polymer layer porosity increase.

It is more expedient for polymer modification to use silica gels with higher pore volume.

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