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Uniform-sized polymer-based separation media prepared using vinyl methacrylate as a cross-linking agent Possible powerful adsorbent for solid-phase extraction of halogenated organic solvents in an aqueous environment

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Abstract

Uniform-sized macroporous polymer-based separation media were prepared through a typical two-step swelling method utilizing vinyl methacrylate or other ordinary cross-linking agents to investigate their properties as packing materials in HPLC. A simple and less hydrophobic cross-linking agent, vinyl methacrylate, afforded stable macroporous packing materials unexpectedly affording the largest retention volume towards hydrophobic solutes in reversed-phase liquid chromatography with good column efficiency. The retention ability towards seven halogenated organic solvents from chloroform to tetrachloroethylene was found to be much higher than that with a typical hydrophobic polymer-based packing material, poly(styrene–divinylbenzene) particles, and also a typical C_{18} silica-based hydrophobic station phase.

1. Introduction

With growing needs for the recovery and/or analyses of environmental organic pollutants such as halogenated organic solvents, various strategies to simplify the pretreatment of environmental samples have been developed [1–3]. Generally, concentration of organic pollutants from aqueous media is necessary because of the low solubility of such compounds in an aqueous phase [4,5]. Recovery of organic pollutants by reversed-phase liquid chromatography (RPLC) using solid-phase extraction has frequently been utilized for pretreatment [1,2,4,5].

From its retention properties in RPLC, a C_{18} stationary phase is one of the most effective adsorbents and various types of C_{18} packing materials are commercially available for utilization in solid-phase extractions. Hydrophobic compounds are effectively concentrated from aqueous media with a C_{18} stationary phase followed by easy recovery of the concentrated compounds by a subsequent flow of an organic solvent such as methanol [1].

Of the available adsorbents for the recovery and analysis of halogenated organic solvents such as chloroform or tetrachloroethylene, a polymer-

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based packing material is more effective than a silica-based packing material [6]. Fig. 1 shows a comparison of separation selectivity towards seven common halogenated organic solvents between a typical monomeric C_{18} packing material and two ordinary polymer-based packing materials, poly(methyl methacrylate–ethylene dimethacrylate) beads (MMA–EDMA) and poly(styrene–divinylbenzene) beads (ST–DVB) [7].

Although MMA–EDMA is considered to be relatively hydrophilic packing material in RPLC, the k' values for the four trihalogenated methanes utilized (chloroform to bromoform) are larger than those with the C_{18} stationary phase. This means that MMA–EDMA affords a higher concentration ratio than the C_{18} stationary phase for the four solutes employed.

Both of the polymer-based packing materials utilized here can separate the four trihalogenated methanes, which cannot be separated with the C_{18} stationary phase, whereas the C_{18} stationary phase easily separates the four trihalogenated methanes from a trihalogenated ethane, which cannot be readily achieved with the polymer-based packing materials. Moreover, the C_{18} stationary phase can hardly separate trichloroethane and trichloroethylene, whereas ST–DVB can easily separate these two compounds, having different molecular planarities. These different separation selectivities between silica- and polymer-based packing materials are of interest for effecting different types of separations such as group separation or isomer separation. Polymer-based separation media are good for isomer separations, and we have been trying to prepare new media or adsorbents to extend their potential utility.

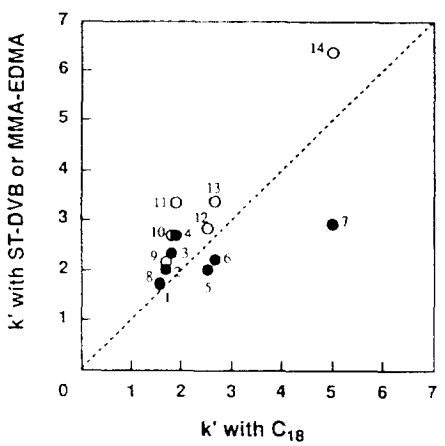

Fig. 1. Separation selectivities towards halogenated organic solvent on ordinary polymer-based packing materials compared with monomeric C_{18} packing material. Solute Nos. 1–7: ● = poly(methyl methacrylate–ethylene dimethacrylate) packing material (MMA–EDMA) versus C_{18} packing material. Solute Nos. 8–14: ○ = poly(styrene–divinylbenzene) packing material (ST–DVB) versus C_{18} packing material. Solutes: 1 = chloroform; 2 = bromodichloromethane; 3 = dibromochloromethane; 4 = bromoform; 5 = 1,1,1-trichloroethane; 6 = trichloroethylene; 7 = tetrachloroethylene; 8 = chloroform; 9 = bromodichloromethane; 10 = dibromochloromethane; 11 = bromoform; 12 = 1,1,1-trichloroethane; 13 = trichloroethylene; 14 = tetrachloroethylene. Chromatographic conditions: mobile phase, 60% aqueous acetonitrile; flow-rate, 0.8 ml/min; detection, UV at 205 nm.

Most synthetic polymer-based separation media have been prepared utilizing a few limited cross-linking agents, which would affect their chromatographic properties. As utliized for the preparation of MMA–EDMA and ST–DVB, relatively reactive ethylene dimethacrylate and divinylbenzene (Fig. 2) are alternatively utilized for the preparation of majority of synthetic hydrophobic polymer-based HPLC packing materials. Therefore, when the copolymerization reactivity between the cross-linking agents and

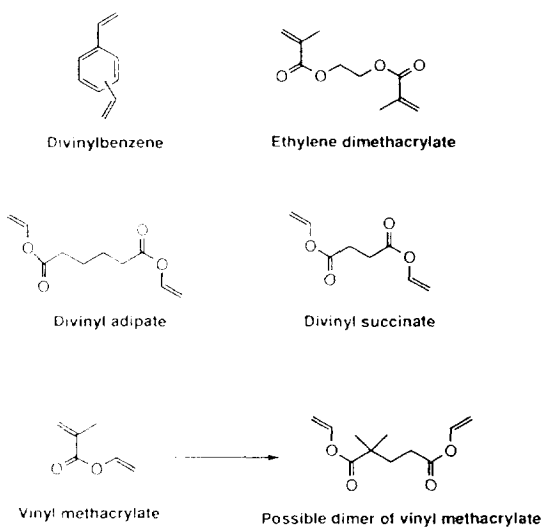

Fig. 2. Structures of cross-linking agents.

comonomers to be incorporated is not well matched, the macroporous copolymer beads obtained will become chemically and/or physically heterogeneous [8]. In severe cases, no comonomers are incorporated in the cross-linked structure owing to the badly mismatched copolymerization [9].

In order to alleviate possible mismatching of the copolymerization of reactive ethylene dimethacrylate or divinylbenzene with less reactive comonomers, we recently prepared macroporous polymer beads utilizing different types of cross-linking agents having lower polymerization reactivities [10]. Divinyl adipate (Fig. 2) was found to show interesting retention properties, but the polymer beads obtained were all unstable gel-type beads, probably owing to the flexible structure and swelling in an aqueous acetonitrile mobile phase, leading to high column pressure drops.

Although the divinyl succinate utilized previously [10] (Fig. 2) afforded stable macroporous beads, the retention properties (hydrophobicity) were not suitable for the purpose to be discussed here, because the hydrophobicity of the beads was lower than that of beads prepared utilizing ethylene dimethacrylate as the cross-linking agent.

In this work, we utilized vinyl methacrylate (Fig. 2) as a cross-linking agent, to overcome the disadvantages encountered when using divinyl adipate and divinyl succinate. Vinyl methacrylate is one of the simplest cross-linking agents, but one of the possible dimers that might be formed by the faster reaction between methacrylate groups compared with vinyl alcohol groups would have an intermediate structure between divinyl succinate and divinyl adipate, with the possibility of overcoming the disadvantages of both of those beads.

2. Experimental

2.1. Materials

Divinyl succinate and vinyl *p-tert.*-butylbenzoate were gifts from Fuso Chemical Industry (Osaka, Japan) and divinyl adipate and vinyl methacrylate were gifts from ShinEtsu Vinyl Acetate (Osaka, Japan). Ethylene dimethacrylate and methyl methacrylate were purchased from Tokyo Chemical Industry (Tokyo, Japan) and Wako (Osaka, Japan), respectively. All the monomers were purified by general distillation techniques in vacuo to remove the polymerization inhibitors. Benzoyl peroxide as a radical initiator was purchased from Nacalai Tesque (Kyoto, Japan) and utilized as received.

2.2. Two-step swelling and polymerization method

Uniformly sized polystyrene seed particles as shape templates were prepared through an emulsifier-free emulsion polymerization and purified by the previously reported method [11]. The size of the seed particle was ca. 1 μm in diameter.

The preparation of uniformly sized macroporous polymer beads by a two-step swelling and polymerization method was carried out as follows. An aqueous dispersion of the uniformly sized polystyrene seed particles (9.5×10^{-2} g/ml) (1.4 ml) was admixed with a microemulsion prepared from 0.95 ml of dibutyl phthalate as activating solvent [12], 0.085 g of benzoyl peroxide, 0.04 g of sodium dodecyl sulfate and 10 ml of distilled water by sonication. This first swelling step was carried out at room temperature while stirring at 125 rpm. Completion of the first swelling step was determined as the vanishing point of micro oil droplets in the microemulsion observed using an optical microscope.

A dispersion of 10 ml of cross-linking agent (or 8 ml of cross-linking agent and 2 ml of comonomer) and 10 ml of cyclohexanol as a parogenic solvent in 90 ml of water containing 1.92 g of poly(vinyl alcohol) (degree of polymerization = 500, saponification value = 86.5–89 mol-%) as a dispersion stabilizer was added to the dispersion of swollen particles. Swelling was carried out at room temperature for 12 h while stirring at 125 rpm.

After the second swelling step was completed, the polymerization procedure was started at 70°C under an argon atmosphere with slow stirring.

After 24 h, the dispersion of polymerized beads was poured into 250 ml of water to remove the poly(vinyl alcohol) suspension stabilizer and the supernatant was discarded after sedimentation of the beads.

The polymer beads were redispersed in methanol and the supernatant was again discarded after sedimentation. This procedure was repeated three times in methanol and twice in tetrahydrofuran (THF), then the polymer beads were filtered on a membrane filter, washed with THF and acetone and dried at room temperature to determine the chemical yields of the beads.

The prepared beads were packed into a stainless-steel column (100 mm × 4.6 mm I.D.) by a slurry technique, using aqueous acetonitrile as the slurry medium, to evaluate their chromatographic characteristics.

2.3. Chromatography

All the chromatographic solvents were purchased from Nacalai Tesque and used as received. HPLC was performed with a Jasco 880-PU Intelligent HPLC pump equipped with a Rheodyne Model 7125 valve loop injector and a Jasco UVIDEC-100-III UV detector set at 254 or 205 nm. Chromatography was carried out at 30 ± 0.5°C and a Shimadzu C-R4A recorder was utilized.

2.4. BET measurements

BET measurements on the prepared beads were carried out at Fuso Chemical Industry (Fukuchiyama, Japan).

3. Results and discussion

3.1. Physical properties of the beads

The physical data for the prepared beads are summarized in Table 1. The beads prepared through homopolymerization of each cross-linking agent were obtained in good chemical yields. As mentioned in the Introduction, the specific surface area of DVAP is severely limited by BET measurement, whereas the pore volume measured by size-exclusion chromatography (SEC) in tetrahydrofuran (THF) resembles those of EDMA and DVSA. This means that DVAP has a gel-type structure which cannot retain a porous structure under the dry conditions required for

Table 1
Properties of the prepared packing materials

Cross-linking agent	Comonomer	Abbreviation	Yield (%)	C (%)[a] (calcd.)	SA[b] (m^2/g)	Pressure[c] (MPa)	Pore volume[d] (ml/g)
Ethylene dimethacrylate	No	EDMA	99	59.48 (60.59)	376.6	2.4	0.656
Divinyl succinate	No	DVSA	98	55.68 (56.47)	204.7	2.7	0.627
Divinyl adipate	No	DVAP	95	60.07 (60.59)	4.7	4.0	0.664
Vinyl methacrylate	No	VMA	95	64.17 (64.27)	300.8	4.4	0.548
Vinyl methacrylate	Methyl methacrylate	VMA–MMA	79	63.14 (63.41)	15.9	4.4	0.540
Vinyl methacrylate	Vinyl *p-tert.*-butylbenzoate	VMA–VPTBBA	93	66.16 (66.70)	320.4	3.4	0.565

[a] Measured by elemental analyses.
[b] SA = specific surface area measured by the BET method.
[c] Pressure = column pressure drop observed in 60% aqueous acetonitrile at 0.8 ml/min. Column size: 100 mm × 4.6 mm I.D.
[d] Measured by SEC in tetrahydrofuran.

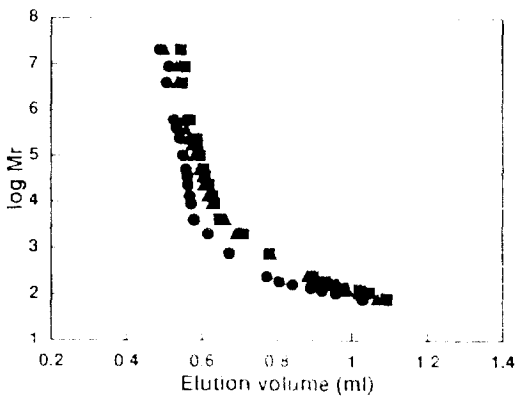

Fig. 3. Calibration graphs for [illegible] beads prepared using vinyl methacrylate as cross-linking agent. ■ VMA; ● VMA/MMA; ▲ VMA/VPTBBA. Chromatographic conditions: mobile phase, tetrahydrofuran; flow rate, 0.5 ml/min; detection, UV at 254 nm; samples, polystyrene standards and alkylbenzenes.

BET measurements. In fact, the calibration graph for DVAP in THF indicated that DVAP has only small pores, which is a typical property of gel-type beads [13].

BET measurements indicated that VMA has a large specific surface area, and a broad pore size distribution is observed from the calibration graph obtained by SEC in THF, as depicted in Fig. 3. These observations suggest that VMA has a stable porous structure, hence the preparation of macroporous beads utilizing vinyl methacrylate overcomes the problem with DVAP mentioned above.

The size monodispersity of VMA appears excellent, as demonstrated in Fig. 4. Whereas DVSA and DVAP show warped shapes (Fig. 4), owing to their relatively slow polymerization rate [14], the shape of VMA is spherical. In detail,

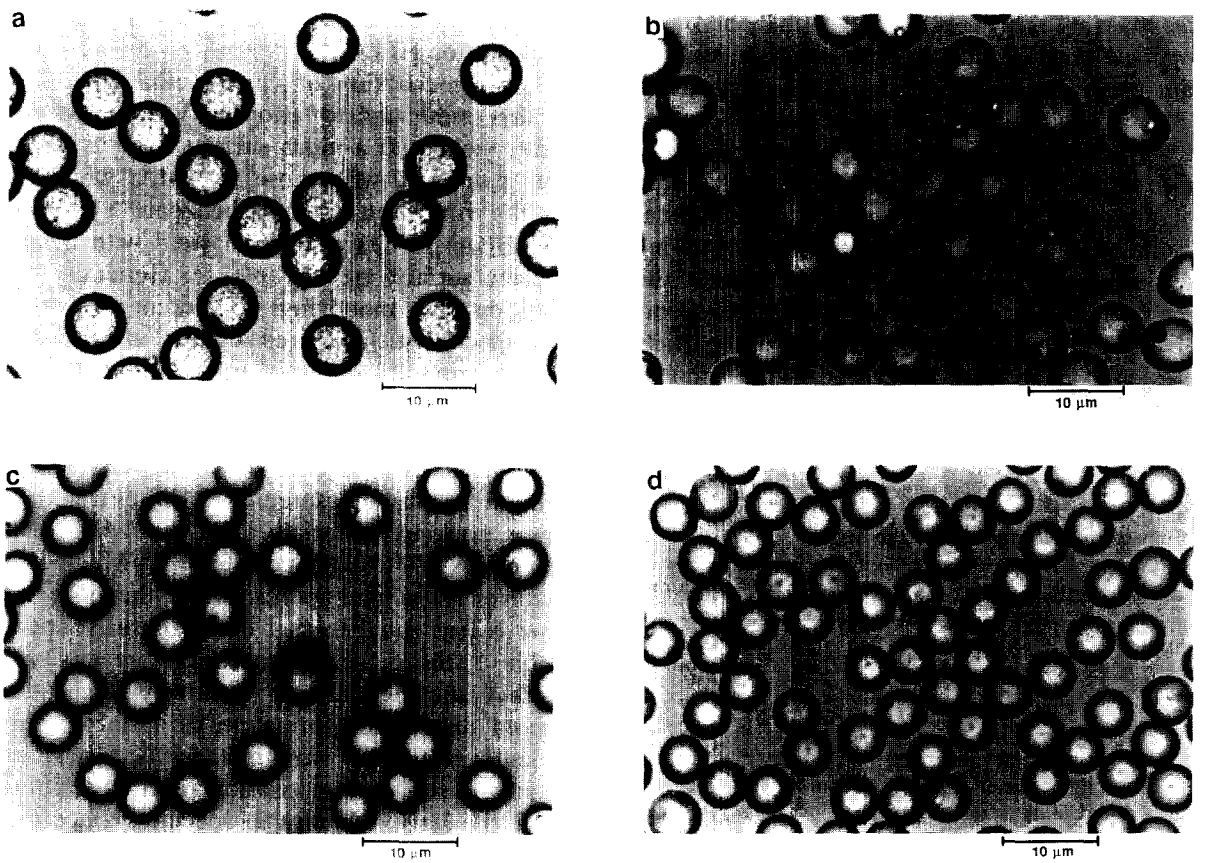

Fig. 4. Optical micrographs of the prepared [illegible] (a) EDMA; (b) DVSA; (c) DVAP; (d) VMA.

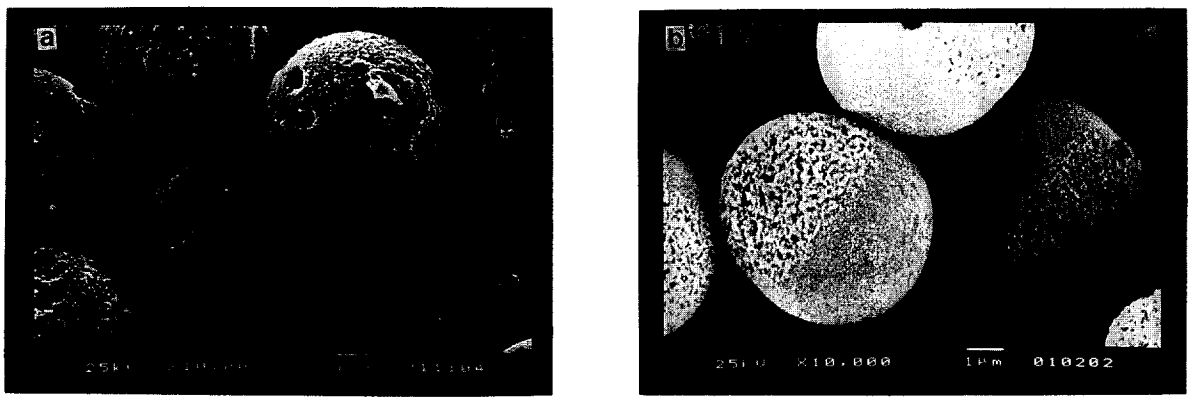

Fig. 5. Scanning electron micrographs of (a) VMA and (b) DVSA.

the scanning electron micrograph of VMA (Fig. 5) exhibits a very rough surface with a few pits and the particle size of the beads obtained is smaller (4.7 μm) than the calculated size of the final particles in the swelling process (5 μm). Moreover, Table 1 also shows that VMA is obtained with a slightly smaller pore volume than other beads. Since the chemical yield of VMA is good and the observed carbon content of VMA is comparable to the calculated value, these reductions in the particle size and pore volume mean that part of the porogenic solvent is somehow lost from the swollen particles during the polymerization step [15]. On the basis of the data obtained, the amount of the porogenic solvent left in a swollen or polymerizing particle is calculated to be 83 vol.-% of the amount introduced. This percentage is equivalent to the decrease in the particle size and the pore volume of the final beads. Although the observed decrease in particle size affords a comparatively higher column pressure drop which is similar to that of gel-type DVAP, the pressure drop was very stable, and the prepared VMA is stable enough to be utilized as a column packing material for HPLC.

Table 2
Chromatographic properties of the beads

Packing material	$k'_{monomer}$ on C_{18}[a]	$\alpha(CH_2)$[b]	$\alpha(T/O^c)$
EDMA	3.63	1.24	1.30
DVSA	1.74	1.17	2.12
DVAP	4.47	1.23	2.26
VMA	2.75	1.32	1.30

[a] k' of each monomer on C_{18} column in 60% aqueous methanol (UV detection at 205 nm).
[b] $k'_{pentylbenzene}/k'_{butylbenzene}$ on each packing material in 60% aqueous acetonitrile.
[c] $k'_{triphenylene}/k'_{o\text{-}terphenyl}$ in 60% aqueous acetonitrile.

Copolymerization of vinyl methacrylate with methyl methacrylate affords (VMA–MMA) a lower yield with a much smaller specific surface area compared with those of VMA, while that with vinyl *p-tert.*-butylbenzoate (VMA–VPTBBA) results in a good yield with a large specific surface area (Table 1). Generally, the addition of a monovinyl comonomer decreases the specific surface area of the macroporous beads through a decrease in the volume in the small pore regions compared with those prepared by homopolymerization of a divinyl monomer cross-linking agent [13]. However, the calibration graphs measured in THF (Fig. 3) on three packing materials (VMA, VMA–MMA and VMA–VPTBBA) indicate that VMA–MMA involves more micropores, while the pore volume is just equal to that of VMA, as found in Table 1. Since the polymerization reactivity of methyl methacrylate is relatively high, this should disturb the formation of a stable cross-linked structure by vinyl methacrylate, having a relatively slow polymerization reactivity. Therefore, the large decrease in specific surface area found in VMA–MMA is due to the formation of a gel-type structure.

On the other hand, copolymerization with the less reactive comonomer vinyl *p-tert.*-butylbenzoate [9] afforded stable macroporous beads with a good yield and a large specific surface area. Since no stable macroporous beads were obtained by copolymerization of divinyl adipate and vinyl *p-tert.*-butylbenzoate or with methyl methacrylate, vinyl methacrylate increases the possible combination of copolymerizations which can afford stable macroporous beads.

3.2. Chromatographic properties of the beads

When the chromatographic separation selectivities of DVSA and DVAP are compared with those of EDMA in the RPLC mode, both DVSA and DVAP show different separation selectivities, as depicted in Fig. 6, where flat aromatic solutes (nos. 7–11) such as pyrene or triphenylene are preferably retained with DVSA and DVAP compared with alkylbenzenes (Nos. 1–6). These tendencies with DVSA and DVAP indicate relatively large α(T/O) ($k'_{\text{triphenylene}}/k'_{o\text{-terphenyl}}$) values, which is usually utilized as a parameter to show molecular recognition of the stationary phase toward flat solutes [16], compared with that with EDMA, as summarized in Table 2. The reason why these differences occur is not clear, but a different polymerization process, including cyclization, might be a possible reason for the effect on the cross-linked structures [14].

As mentioned in the Introduction, DVSA affords smaller retention volumes for the solutes used, probably owing to the lower carbon content of the monomer, which would reduce the hydrophobicity of the stationary phase in RPLC. The k' value of divinyl succinate monomer measured with a C_{18} stationary phase is the smallest for all the cross-linking agents. On the other hand, DVAP shows much larger retention volumes than EDMA. In this case, the k' value of divinyl adipate monomer is 1.2 times larger than that of ethylene dimethacrylate monomer, in spite of the identical carbon contents. This clearly means that both the hydrophobicity of the monomer and the carbon content play an important role in affecting the retention volume of the polymer beads in RPLC.

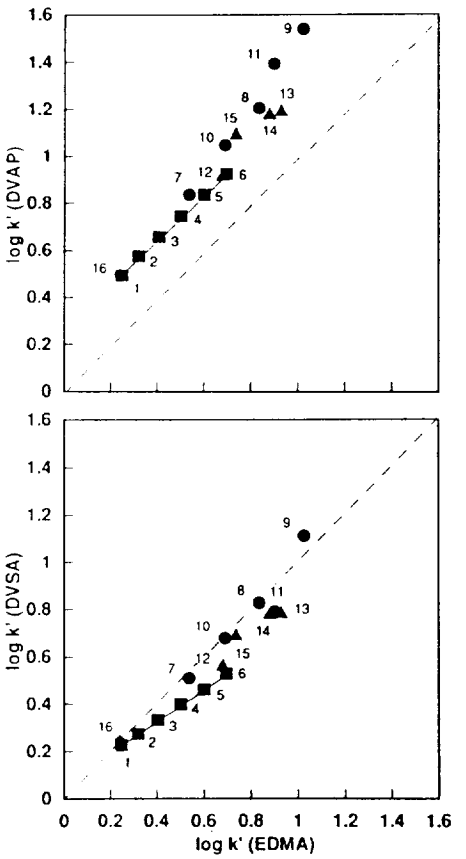

Fig. 6. Comparison of separation selectivities on polymer-based separation media. Solutes: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = propylbenzene; 5 = butylbenzene; 6 = pentylbenzene; 7 = naphthalene; 8 = anthracene; 9 = triphenylene; 10 = fluorene; 11 = pyrene; 12 = diphenylmethane; 13 = triphenylmethane; 14 = *o*-terphenyl; 15 = triptycene; 16 = nitrobenzene. Chromatographic conditions: mobile phase, 60% aqueous acetonitrile; flow-rate, 0.8 ml/min; detection, UV at 254 nm.

VMA shows a better column efficiency than DVSA and DVAP for the separation of alkylbenzenes in 60% aqueous acetonitrile. The chromatogram with VMA is presented in Fig. 7 [7]. The separation selectivities of VMA were compared with other polymer-based packing materials as discussed above and depicted in Fig. 8. Although vinyl methacrylate monomer has the second smallest k' on the C_{18} stationary phase

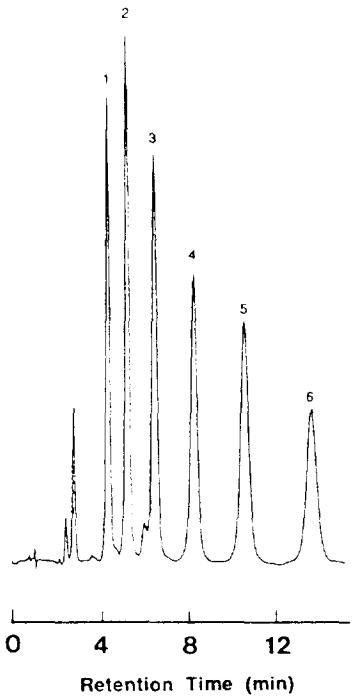

Fig. 7. Chromatogram for the separation of alkylbenzenes with VMA. Chromatographic conditions: column size, 100 mm × 4.6 mm I.D.; mobile phase, 60% aqueous acetonitrile; flow-rate, 0.8 ml/min; detection, UV at 254 nm.

(Table 2) in spite of having the highest carbon content, VMA unexpectedly affords much larger retention volumes even than DVAP, consisting of a more hydrophobic monomer. As also indicated in Table 2, the $\alpha(CH_2)$ value of VMA is the largest and the $\alpha(T/O)$ value is the smallest. This is useful because the predicted possible dimeric structure of vinyl methacrylate resembles those of divinyl succinate and divinyl adipate, but the separation selectivity observed is similar to that with EDMA.

Finally, if the capacity factors of the seven halogenated organic solvents with VMA are compared with those of common hydrophobic separation media, VMA affords a much larger retention than ST–DVB and C_{18} stationary phases, as shown in Fig. 9. This simply means that VMA will afford a much higher concentration ratio than the other stationary phases, which is one of the targets of this work. The separation selectivity of VMA is very similar to

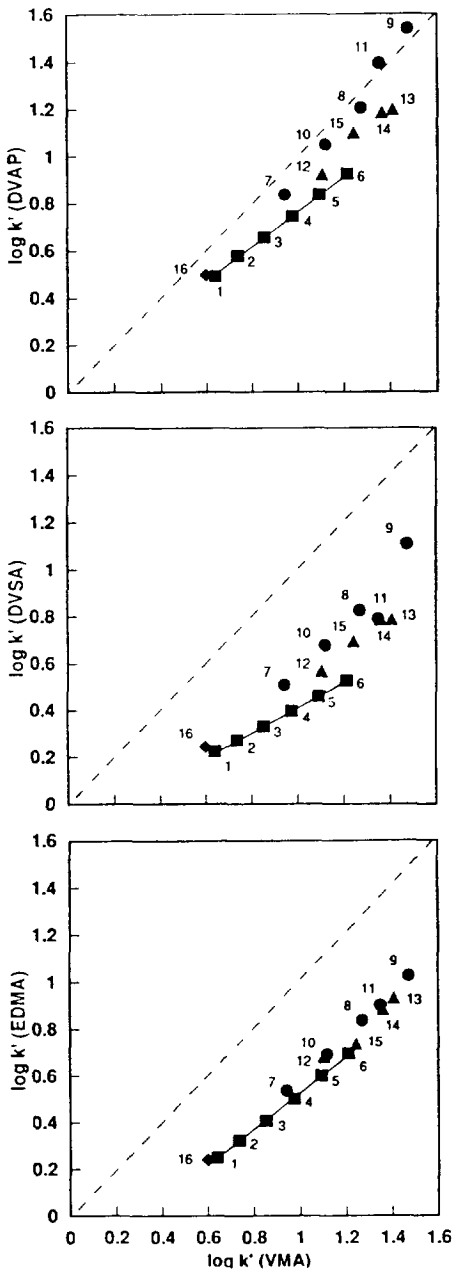

Fig. 8. Comparison of separation selectivities on polymer-based separation media. Solutes: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = propylbenzene; 5 = butylbenzene; 6 = pentylbenzene; 7 = naphthalene; 8 = anthracene; 9 = triphenylene; 10 = fluorene; 11 = pyrene; 12 = diphenylmethane; 13 = triphenylmethane; 14 = *o*-terphenyl; 15 = triptycene; 16 = nitrobenzene. Chromatographic conditions: mobile phase, 60% aqueous acetonitrile; flow rate, 0.8 ml/min; detection, UV at 254 nm.

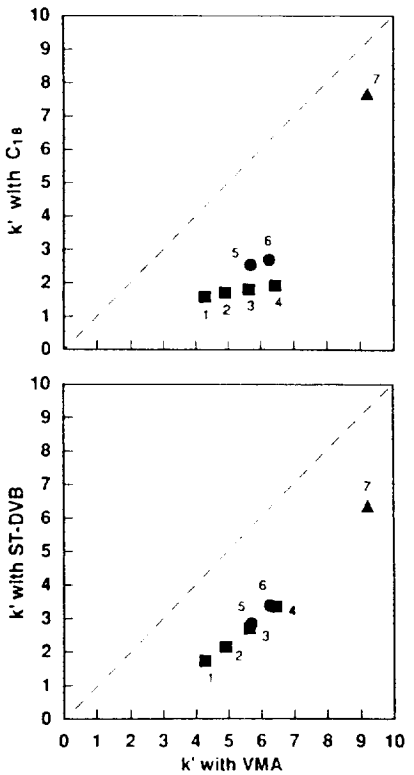

Fig. 9. Comparison of separation selectivities toward halogenated organic solvent with polymer- and silica-based packing materials. Chromatographic conditions: mobile phase, 60% aqueous acetonitrile; flow-rate, 0.8 ml/min; detection, UV at 205 nm. Solutes: 1 = chloroform; 2 = bromodichloromethane; 3 = dibromochloromethane; 4 = bromoform; 5 = 1,1,1-trichloroethane; 6 = trichlorethylene; 7 = tetrachloroethylene.

those of ST–DVB, which means that the separation selectivity of polymer-based separation media is retained. As mentioned before, EDMA rather than DVSA or DVAP shows a similar separation selectivity to VMA, and therefore the retention volume, which is one of the most important parameters of adsorbents for solid-phase extraction, can be enhanced using vinyl methacrylate.

4. Conclusion

Vinyl methacrylate afforded stable macroporous separation media with good size monodispersity. Although the monomer utilized has a simple and hydrophilic structure, the polymer beads prepared unexpectedly show a much larger retention volume than common hydrophobic separation media which have been utilized as commercial adsorbents for solid-phase extractions. So far, detailed investigations have not been completed, but the chromatographic properties obtained with VMA are of interest and useful for the preparation of a new variety of stationary phases and adsorbents.

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