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Preparation and chromatographic properties of uniform size cross-linked macroporous poly(vinyl *p-tert.*-butylbenzoate) beads

Evaluation of preferential retention toward organohalides

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ABSTRACT

Uniform size cross-linked macroporous poly(vinyl *p-tert.*-butyl benzoate) beads (VPTBBA) were prepared by a two-step swelling and polymerization method. VPTBBA was obtained in 78% yield and utilized as a packing material in high-performance liquid chromatography. The specific surface area of VPTBBA, which had a polymodal broad pore size distribution, was calculated as 314 m^2/g by the BET method. In the reversed-phase mode, VPTBBA showed preferential retention towards some aromatic and/or aliphatic halogenated compounds. In a comparison of its chromatographic properties with those on other packing materials such as two kinds of poly(vinyl carboxylate)-based beads, poly(styrene–divinylbenzene) beads and poly(methyl methacrylate–ethylene dimethacrylate) beads, and a silica-based monomeric C_{18} stationary phase, the selectivities on VPTBBA can be explained mainly based on both dipole–dipole interactions caused by the π-acidic phenyl group of VPTBBA and preferential retention towards planer solutes. Moreover, the relatively hydrophobic *tert.*-butyl groups contribute to steric selectivity and to the total hydrophobicity of the packing material.

INTRODUCTION

Halogenated organic compounds are one of the most serious environmental contaminants because they possibly cause cancer, deformity or at least health disorders [1–7]. Therefore, attempts have been made to remove organohalides such as dioxins from the environment [8–13]. Toxic chlorinated dibenzo-*p*-dioxins (PCDDs) are photodecomposed using various techniques to produce less toxic compounds [14–20] and the removal of halogenated alkanes or alkenes utilized as dry-cleaning solvents such as chloroform, trichloroethane and tetrachloroethylene from air and environmental water has also been attempted [21], but for efficient operation it is necessary to concentrate these toxic pollutants from the environmental media because their concentrations are usually low, especially in aqueous media [22].

Recently, a slightly cross-linked polymer of vinyl *p-tert.*-butyl benzoate was reported to show preferential absorption of organohalides such as chloroform and tetrachloroethylene [23]. A soft gel, Chloroclean, is now commercially available for the absorption of organohalides. This monomer is chromatographically interesting because it contains an aromatic ester group with a bulky

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and hydrophobic *tert.*-butyl substituent at the *para* position of the phenyl ring.

Here, we report on the preparation of a size monodisperse HPLC packing material of cross-linked poly(vinyl *p-tert.*-butyl benzoate) beads (VPTBBA) utilizing a two-step swelling and polymerization method [24] and its chromatographic properties in comparison with typical polymer packing materials such as poly(styrene–divinylbenzene) particles (ST) and poly(methyl methacrylate–ethylene dimethacrylate) particles (MMA) and also a typical silica-based stationary phase such as a C_{18} phase. Moreover, two other kinds of cross-linked poly(vinyl carboxylate)s were utilized as reference packing materials for comparison of their chromatographic properties with those of VPTBBA.

EXPERIMENTAL

Materials

Vinyl *p-tert.*-butylbenzoate (CAS No. 15484-80-7) and vinyl cyclohexanecarboxylate were gifts from Fuso Chemical (Osaka, Japan) and vinyl benzoate was purchased from Polyscience (Warrington, PA, USA). A methanol solution of standard halogenated compounds, "Organohalides Std. Soln. A", was purchased from Wako (Osaka, Japan) and all other solutes except tetrachlorodibenzo-*p*-dioxins (TCDDs) were purchased from Nacalai Tesque (Kyoto, Japan). Styrene, divinylbenzene (55% grade), methyl methacrylate and ethylene dimethacrylate were also purchased from Nacalai Tesque.

Preparation of six monodisperse polymer beads

Polystyrene seed particles were prepared by an emulsifier-free emulsion polymerization method reported elsewhere [25]. A two-step swelling and polymerization method took place using dibutyl phthalate as an activating solvent (first-step swelling) followed by further swelling with monomers including porogenic solvent (second-step swelling) at room temperature [26]. The ratio of monomer, cross-linking agent and porogenic solvent was 25:25:50 (v/v/v). Polymerization was carried out at 80°C under an argon atmosphere for 24 h and extraction of porogenic solvent (toluene or cyclohexanol) was carried out by repeated washing with methanol, tetrahydrofuran and toluene. The specific surface area was measured by a Porous Materials automated BET machine and the mercury intrusion method was examined using a Porous Materials Model 60K-A-1 automated porosimeter. These measurements were carried out at the Department of Chemistry, Cornell University (Ithaca, NY, USA) with the permission of Professor Jean M.J. Fréchet.

Chromatography

All chromatographic solvents were purchased from Nacalai Tesque and used without further purification. The polymer particles were packed into a stainless-steel column 100 or 150 mm × 4.6 mm I.D.) using the slurry method. HPLC was performed with a Jasco, 880-PU intelligent pump or a Shimadzu, LC-4A ternary gradient pump equipped with a Rheodyne Model 7125 valve loop injector. Peak monitoring was carried out with a Jasco UVIDEC-100-III or a Shimadzu SPD-2A UV detector set at 254 or 280 nm and with a refractive index detector. Peak information was recorded with Shimadzu C-R4A and C-R3A Chromatopacs. The reproducibility of retention time in duplicate was better than 2%. Polystyrene standard samples for size-exclusion chromatography were purchased from Polymer Laboratories.

Separation of tetrachlorodibenzo-p-dioxins (TCDDs)

Separations of TCDDs were carried out at the Centers for Disease Control (CDC) (Atlanta, GA, USA) using a Waters HPLC system and detection was carried out at 230 nm. All the TCDDs were used with permission of Dr. Donald G. Patterson, Jr. (CDC).

RESULTS AND DISCUSSIONS

Preparation of size monodisperse particles

In addition to the poly[vinyl *p-tert.*-butylbenzoate (1)–ethylene dimethacrylate] packing (VPTBBA), poly[vinyl benzoate (2)–ethylene dimethacrylate] (VBA) and poly[vinyl cyclohexanecarboxylate (3)–ethylene dimethacrylate] packings (VCHA) were also prepared as refer-

TABLE I

CHEMICAL YIELDS OF THE PREPARED PARTICLES

Monomer	Cross-linker	Porogen	Yield (%)	Abbreviation
1[a]	EDMA[b]	Toluene	78	VPTBBA
2[a]	EDMA[b]	Toluene	79	VBA
3[a]	EDMA[b]	Toluene	72	VCHA
Styrene	DVB[c]	Cyclohexanol	91	ST
Methyl methacrylate	EDMA[b]	Cyclohexanol	95	MMA

[a] See Fig. 1.
[b] Ethylene dimethacrylate.
[c] Divinylbenzene.

ence packing materials. The structures of the monomers utilized are depicted in Fig. 1. The volume ratio of monomers, porogen and other additives and the polymerization conditions were identical. However, with vinyl *p-tert.*-butylbenzoate, it took 24 h to complete the swelling, whereas with vinyl benzoate and vinyl cyclohexanecarboxylate only 2–4 h were required.

Yields calculated based on the amounts of the monomers including cross-linking agent utilized in the swelling step were less than 80% (Table I). These yields are relatively lower than those of the prepared poly(styrene–divinylbenzene) particles (ST) or poly(methyl methacrylate–ethylene dimethacrylate) particles (MMA), which gave quantitative yields [27]. These findings can be explained by the difference in copolymerization reactivity ratio between ethylene dimethacrylate and vinyl carboxylates. For example, the copolymerization reactivity ratio between a monomer with methyl methacrylate (M_1) and vinyl *p-tert.*-butylbenzoate (M_2) are reported to be 20.07 and 0.0565 for r_1 and r_2, respectively [23]. The difference means that at an early stage of the polymerization, preferential polymerization between ethylene dimethacrylates as depicted in eqn. 1 [28] takes place, resulting in a low content of vinyl *p-tert.*-butylbenzoate in the cross-linked polymer.

vinyl *p-tert.*-butylbenzoate·
+ ethylene dimethacrylate (easy)
vinyl *p-tert.*-butylbenzoate·
+ vinyl *p-tert.*-butylbenzoate (difficult)
ethylene dimethacrylate·
+ vinyl *p-tert.*-butylbenzoate (difficult)
ethylene dimethacrylate·
+ ethylene dimethacrylate (easy) (1)

On the basis of elemental analysis data (Table II), the experimentally obtained mole ratio of

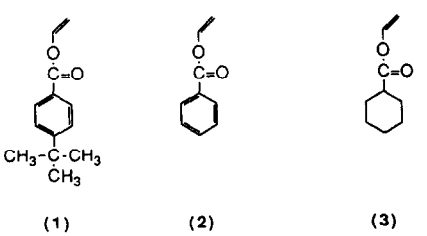

Fig. 1. Structures of monomers.

TABLE II

ELEMENTAL ANALYSIS OF PARTICLES

Packing material	H (%)	C (%)	O (%)
VPTBBA	7.34	64.08	28.58
VBA	6.48	62.97	30.55
VCHA	7.71	62.20	30.09
ST	8.08	90.65	–
MMA	7.37	59.03	33.60

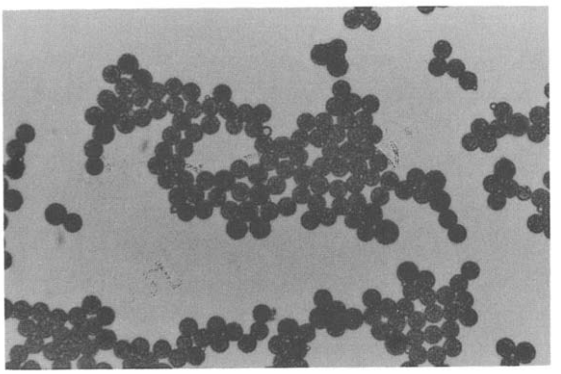

Fig. 2. Optical micrograph of VPTBBA (×450).

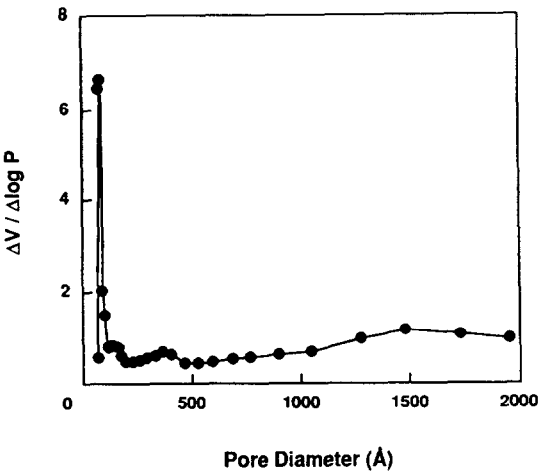

Fig. 3. Pore size distribution of VPTBBA measured by mercury intrusion method.

the polymerized vinyl *p-tert.*-butylbenzoate and ethylene dimethacrylate was calculated as 3:7. As the theoretical mole ratio should be 5:5, a loss of vinyl *p-tert.*-butylbenzoate resulted in relatively low yield of VPTBBA. Good monodispersity of VPTBBA was obtained as shown in Fig. 2. The estimated particle diameter of VPTBBA was *ca.* 5.6 μm.

Surface area and pore size

The specific surface areas of the three particles measured by the BET method are summarized in Table III. All three particles were found to have similar specific surface areas. The calculated average pore size of VPTBBA measured by the mercury intrusion method is around 80 Å, but the volume percentage of the pores smaller than 100 Å was about 50%, as depicted schematically in Fig. 3. Interestingly, the mercury porosimetry also suggested that VPTBBA also involved very large pores up to 2000 Å, the volume percentage of the pores between 500 and 2000 Å being calculated as 30% (Fig. 3). These findings suggest that VPTBBA has a polymodal relatively broad pore size distribution, which is the cause of the very rough surface observed in the SEM picture of VPTBBA (Fig. 4). This polymodal broad pore structure may be explained also based on the difference in copolymerization reactivity ratio as described in the previous section. In the early stage of polymerization, primary globules with a greater extent of cross-linking were produced. Then, as polymerization proceeded, lower cross-linked polymers including more vinyl *p-tert.*-butylbenzoate were formed

TABLE III

PHYSICAL PROPERTIES OF PARTICLES

Measured by BET method.

Particle	Surface area (m^2/g)	Average pore diameter (Å)
VPTBBA	313.9	60.3
VBA	344.4	61.1
VCHA	410.9	60.3

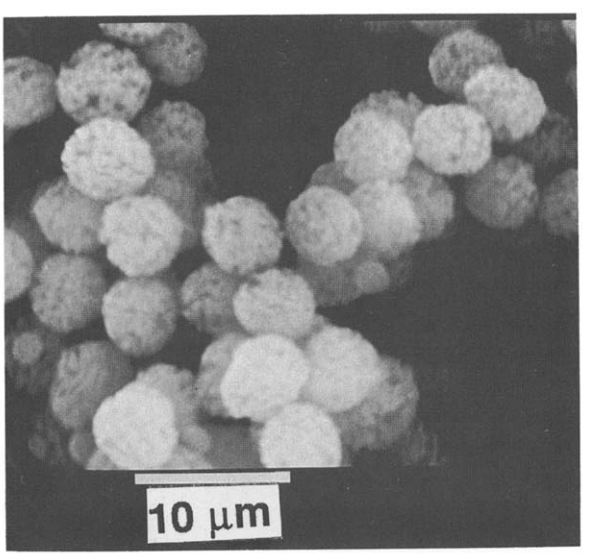

Fig. 4. Scanning electron micrograph of VPTBBA.

to afford the secondary beads which might produce the relatively broad pore size distribution of VPTBBA.

The BET and a mercury intrusion method are usually carried out under dry conditions. Therefore, sometimes, these tend to be incompatible with the results determined by size-exclusion chromatography, which is performed in a swollen condition. This time, tetrahydrofuran (THF) was utilized as the solvent in size-exclusion chromatography. A calibration graph obtained with polystyrene standards and alkylbenzenes on VPTBBA confirms the relatively broad pore size and pore size distribution (Fig. 5) which is basically compatible with the BET and mercury intrusion methods.

Selectivity in reversed-phase mode

VPTBBA separated alkylbenzenes well using 60% aqueous acetonitrile with a 100-mm column, as shown in Fig. 6. If the hydrophobic selectivity of VPTBBA in terms of the increase in retention caused by one methylene group of an alkylbenzene, $\alpha(CH_2)$, is compared with those of VBA, VCHA, ST and MMA [29], VPTBBA has an intermediate hydrophobicity between those of ST and MMA (Table IV). This finding can be expected from elemental analysis data because VPTBBA also has an intermediate carbon content between those of ST and MMA. Interestingly, VPTBBA has almost the same $\alpha(CH_2)$ value as VCHA with a lower carbon content, but a higher $\alpha(CH_2)$ value than VBA. These findings may be explained based on the

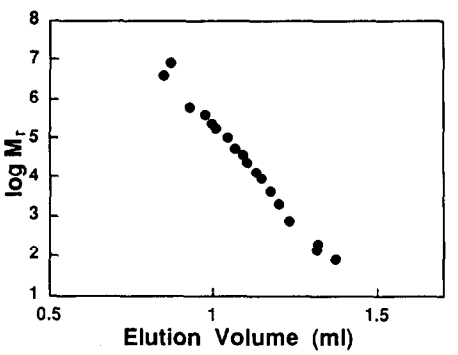

Fig. 5. Calibration graph for VPTBBA. Mobile phase, tetrahydrofuran; flow-rate, 0.5 ml/min; detection, UV at 254 nm. Samples: polystyrene standards and alkylbenzenes.

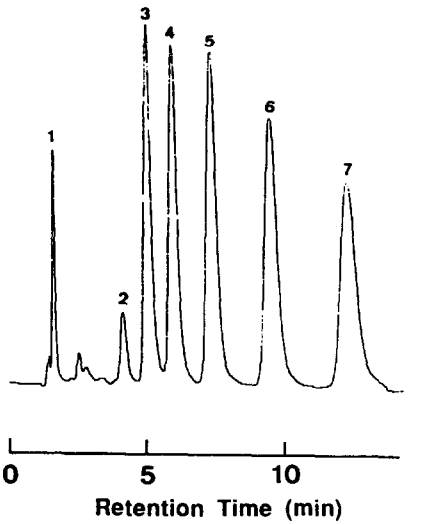

Fig. 6. Separation of alkylbenzenes on VPTBBA. Mobile phase, 60% aqueous acetonitrile; flow-rate, 0.8 ml/min; column, 100 mm × 4.6 mm I.D.; detection, UV at 254 nm. Samples: 1 = uracil; 2 = benzene; 3 = toluene; 4 = ethylbenzene; 5 = propylbenzene; 6 = butylbenzene; 7 = amylbenzene.

difference in contributions between the hydrophobicity of the aromatic ring of VPTBBA and that of the aliphatic ring of VCHA, which is usually more hydrophobic than corresponding aromatic group [30] and the relatively hydrophobic *tert.*-butyl substituent on VPTBBA. Therefore, the *tert.*-butyl substituent is found to contribute the hydrophobicity of the packing material, as expected from a hydrophobic substituent.

On the other hand, steric selectivity in terms of the α value of the planar triphenylene and sterically bulky and similarly hydrophobic *o*-terphenyl (T/O) [29] suggests that VPTBBA shows a much higher steric selectivity than VCHA and MMA, which do not contain a phenyl ring. The α value of VPTBBA is smaller than that of ST because ST includes an aromatic cross-linking agent (divinylbenzene) in addition to the monomer, but the phenyl ring of VPTBBA clearly enhances the steric selectivity. Interestingly, the *tert.*-butyl substituent on VPTBBA also contributes steric selectivity to give a higher α value than VBA. Although micropores have been reported to affect preferential retention towards planar compounds [31], this time VPTBBA,

TABLE IV

CHROMATOGRAPHIC PROPERTIES OF POLYMER BEADS

Mobile phase, 60% acetonitrile; flow-rate, 0.8 ml/min; detection, UV at 254 nm.

Parameter	VPTBBA	VBA	VCHA	ST	MMA
$\alpha(CH_2)^a$	1.31	1.27	1.32	1.49	1.23
T/O^b	2.13	2.03	1.62	2.79	1.27

[a] k'(amylbenzene)/k'(butylbenzene).
[b] k'(triphenylene)/k'(*o*-terphenyl).

VBA and VCHA, which were prepared using almost the same reaction conditions, all produced similar pore structures judging from BET measurements (Table III), and therefore the higher steric selectivity on VPTBBA may be due to not only the phenyl ring but also a contribution of the *tert.*-butyl substituent. Although a *tert.*-butyl substituent is sterically bulky, this finding can be understood if the bulky substituent tends to prevent self-stacking of phenyl rings but enhances interactions between the stationary phase and solutes.

The retention selectivity of VPTBBA in 60% aqueous acetonitrile was compared with those of other packing materials including a silica-based monomeric C_{18} stationary phase (Fig. 7). VPTBBA showed a similar selectivity to VCHA, as expected from the similar $\alpha(CH_2)$ values, except for alkyl alcohols. Although VCHA had almost the same $\alpha(CH_2)$ value as VPTBBA, the preferential retention toward alkyl alcohols on VCHA is probably due to the higher content of hydrophilic oxygen atoms of VCHA than that of VPTBBA. On the other hand, VPTBBA was found to show preferential retention towards hydrophobic solutes such as alkylbenzenes, alkyl bromides and alkanes compared with VBA. This is due to the hydrophobic aliphatic substituent (*tert.*-butyl group) of VPTBBA, as suggested before.

ST showed a longer retention towards all the alkyl alcohols, alkylbenzenes and alkyl bromides tested, including other halogenated compounds (Organohalides Std. Soln. A), which will be described later. However, VPTBBA showed a relatively preferential retention toward hydrophilic alkyl alcohols in comparison with another hydrophobic solutes, which was a different phenomenon from the relationship with the other four stationary phases. As mentioned before, VPTBBA includes an oxygen atom in its structure and this may produce this selectivity. Both MMA and C_{18} stationary phases showed much longer retention toward alkyl alcohols; on the other hand, VPTBBA showed preferential retention towards hydrophobic solutes compared with MMA and C_{18} stationary phases, especially towards alkyl bromides. Interestingly, the retentions of halogenated solutes in Organohalides Std. Soln. A were found to be similar on both VPTBBA and C_{18}, in contrast to those of alkyl alcohols. This finding supports the reported characteristics of VPTBBA described in the Introduction. This kind of tendency was also found between VPTBBA and MMA. In addition, the shorter alkyl chain in the alkyl bromides, the more preferential is the retention shown by VPTBBA. This finding means VPTBBA potentially has a preferential retention with the bromine substituent itself.

Retention selectivity on VPTBBA for substituted benzene derivatives is depicted in Fig. 8 in a comparison with that on ST. Although the phenyl ring of VPTBBA involves both an electron-withdrawing group, a carbonyl group and an electron-donating group (*tert.*-butyl), VPTBBA showed preferential retention towards electron-rich substituted benzene derivatives such as phenol and bromobenzene. On the other hand, ST involving an electron-rich phenyl ring showed preferential retention toward relatively electron-poor substituted benzene derivatives

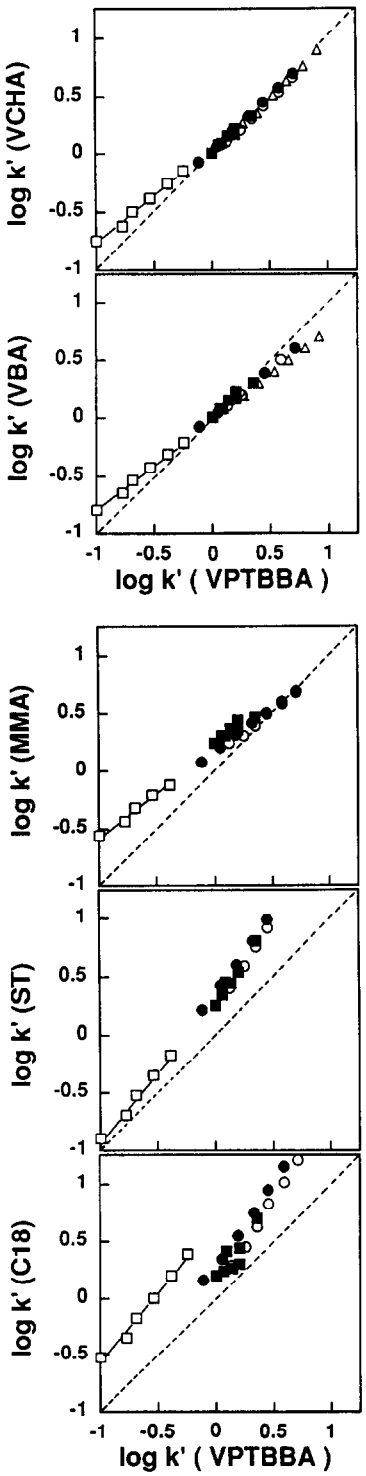

Fig. 7. Selectivity of VPTBBA. Chromatographic conditions in Fig. 6. Samples: □ = alkyl alcohols; ○ = alkylbenzenes; ● = alkyl bromides; ■ = organohalides; △ = alkanes.

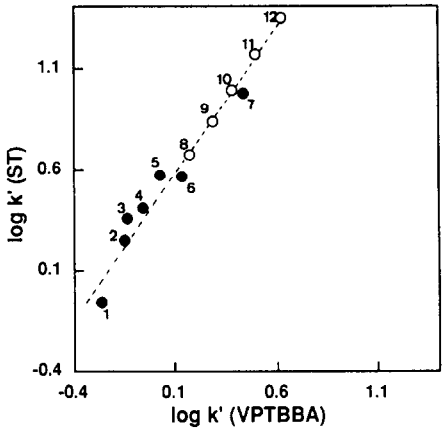

Fig. 8. Selectivity of VPTBBA. Chromatographic conditions as in Fig. 6. Samples: 1 = phenol; 2 = aniline; 3 = acetophenone; 4 = benzonitrile; 5 = methyl benzoate; 6 = nitrobenzene; 7 = bromobenzene; 8 = benzene; 9 = toluene; 10 = ethylbenzene; 11 = propylbenzene; 12 = butylbenzene.

such as acetophenone, benzonitrile and methyl benzoate, with the only exception of nitrobenzene. These findings suggest that VPTBBA tends to act as a stationary phase with an alternatively π-acidic characteristic ligand.

Separation selectivity with organohalides

Retentions of halogenated organic compounds contained in commercial Organohalides Std. Soln. A are summarized in Table V. The standard solution includes seven organohalides with different concentrations which is usually utilized as a standard for gas chromatographic analyses. The compounds are arranged in order of increasing k' values on VPTBBA.

The k' values increased with increase in the number of halogen substituents and carbons of the solutes. Hence chloroform showed the smallest k' value, while tetrachloroethylene gave the largest k' value on every stationary phase. As expected, ST and C_{18} stationary phases showed longer retentions toward all the halogenated compounds owing to their highly hydrophobic characteristics; in addition, interestingly, MMA also showed longer retentions than the more hydrophobic VPTBBA. However, the ratio between k'(chloroform) and k'(tetrachloroethylene) was 1.71 on MMA, which was the smallest selectivity observed. This finding means that

TABLE V

RETENTION PROPERTIES OF ORGANOHALIDES IN ORGANOHALIDES STD. SOLN. A

Mobile phase: 60% aqueous acetonitrile; flow-rate, 0.8 ml/min; detection, refractive index.

No.	Solute	k'					
		VPTBBA	VBA	VCHA	ST	MMA	C_{18}
1	Chloroform	1.02	0.99	1.00	1.72	1.70	1.59
2	Bromodichloromethane	1.21	1.18	1.18	2.14	1.99	1.71
3	1,1,1-Trichloroethane	1.25	1.16	1.19	2.83	1.98	2.55
4	Chlorodibromomethane	1.43	1.40	1.40	2.69	2.31	1.82
5	Trichloroethylene	1.61	1.44	1.46	3.38	2.21	2.70
6	Bromoform	1.67	1.65	1.60	3.35	2.68	1.93
7	Tetrachloroethylene	2.35	2.01	2.07	6.35	2.91	5.02
	α (7/1)[a]	2.30	2.03	2.07	3.69	1.71	3.15
	α (5/3)[b]	1.29	1.24	1.22	1.19	1.11	1.06

[a] k'(tetrachloroethylene)/k'(chloroform).
[b] k'(trichloroethylene)/k'(1,1,1-trichloroethane).

MMA has a relatively preferential retention with the halogenated organic compounds, but the retention selectivity is poor, which should lead to poor resolution. Although ST and C_{18} showed a larger ratio than VPTBBA between k'(chloroform) and k'(tetrachloroethylene), both VBA and VCHA showed smaller ratios than VPTBBA.

The C_{18} stationary phase can separate the halogenated compounds well, except for 1,1,1-trichloroethane and trichloroethylene, as depicted in Fig. 9. These two compounds involve

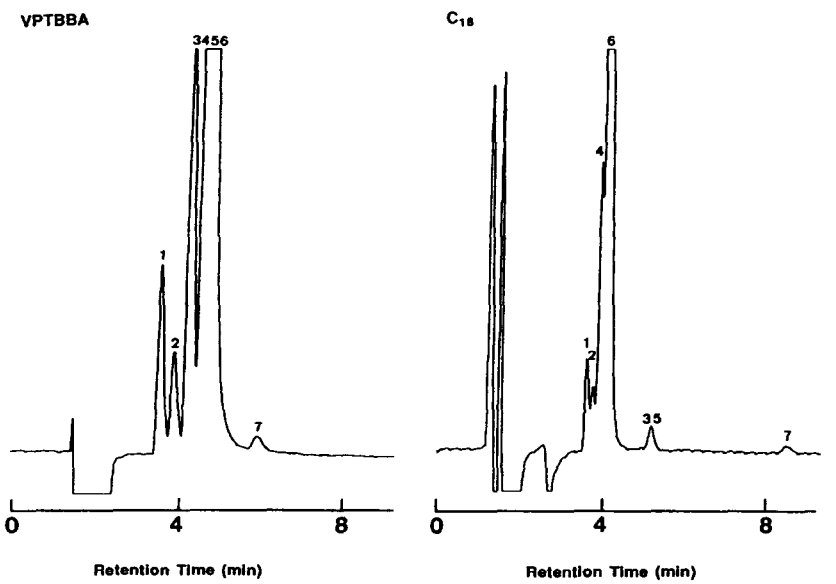

Fig. 9. Separation of organohalide standards. Chromatographic conditions as in Fig. 6, except detection (refractive index). Samples: 1 = chloroform (2 mg/ml); 2 = bromodichloromethane (1 mg/ml); 3 = 1,1,1-trichloroethane (0.1 mg/ml); 4 = chlorodibromomethane (4 mg/ml); 5 = trichloroethylene (0.5 mg/ml); 6 = bromoform (20 mg/ml); 7 = tetrachloroethylene (0.2 mg/ml).

the same number of chlorine substituents but a difference is found in the planarity of the compounds. As the C_{18} stationary phase can separate solutes mainly due to the difference in their hydrophobicity, in this instance a poor resolution of above two compounds is obtained. On the other hand, VPTBBA separated the two compounds well (Fig. 9). If the ratios between k'(1,1,1-trichloroethane) and k'(trichloroethylene) are compared, VPTBBA shows the highest ratio with all six stationary phases. In summary, VPTBBA has a better steric selectivity with a moderate absolute retention towards the halogenated compounds.

Separations of tetrachlorodibenzo-*p*-dioxins (TCDDs) were carried out utilizing acetonitrile as mobile phase. This mobile phase is too strong to separate TCDDs on the usual silica-based stationary phases [32], and therefore polymer-based separation media potentially have longer retentions with TCDDs, so it is suitable for the concentration of TCDDs from aqueous media. As shown in Fig. 10, VPTBBA could separate a synthetic isomer pair, 1,2,3,7-TCDD and 1,2,3,8-TCDD, which are usually difficult to separate, whereas ST could not separate them with much longer retention times. As we reported previously [32], silica-based stationary phase with a π-acidic phenyl ring such as a nitrophenyl group (NPE phase) could separate this isomer pair with the same elution order,

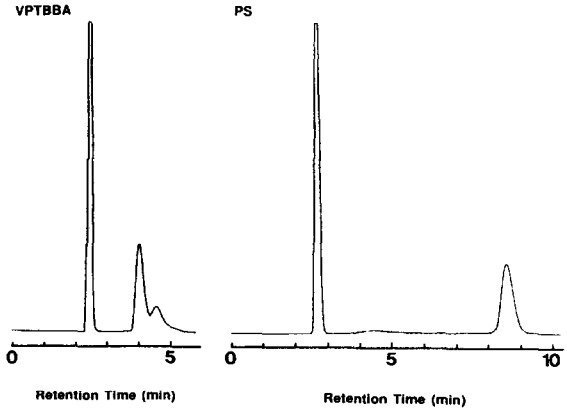

Fig. 10. Separation of a TCDD isomer pair. Mobile phase, acetonitrile; flow-rate, 1 ml/min; detection, UV at 230 nm; column, 150 mm × 4.6 mm I.D. Samples: 1,2,3,7- and 1,2,3,8-TCDD isomer pair.

whereas that with a π-basic ligand such as a pyrenyl group (PYE phase) could not separate them. In this way, as described in the previous section (Fig. 8), VPTBBA acts as a stationary phase with a π-acidic ligand whereas ST has a π-basic ligand.

The retention selectivities of 22 isomers of TCDDs are summarized in Table VI. Although VPTBBA only separated the isomer pair of 1,2,3,7- and 1,2,3,8-TCDDs, ST separated other isomer pairs with much longer retention times. As described before, the selectivity on ST is very similar to those on a silica-based PYE phase and a C_{18} stationary phase but not the same, whereas VPTBBA shows a similar selectivity to silica-based NPE stationary phase in the case of only the isomer pair of 1,2,3,7- and 1,2,3,8-TCDDs. Interestingly, VCHA showed a very similar selec-

TABLE VI

SEPARATION OF TCDDS ON POLYMER-BASED COLUMNS

Mobile phase, acetonitrile; flow-rate, 1 ml/min; detection, UV at 230 nm.

TCDD	k'		
	VPTBBA	ST	VCHA
1234	0.98	4.38	0.8
1236	1.11	4.71	0.97
1239		4.13	
1237	1.21	4.86	1.04
1238	1.55		1.33
1246	0.94	4.09	0.86
1249			
1247	1.05	4.62	0.94
1248			
1267	0.92	4.55	0.98
1289		4.06	
1268	1.10	4.78	0.97
1279		4.19	
1368	1.07	4.27	0.94
1379		4.99	
1469	0.78	3.21	1.06
1269	0.94	3.82	0.84
1478	1.10	4.77	0.97
1278	1.29	6.24	1.08
1369	0.94	4.07	0.86
1378	1.26	5.75	1.05
2378	1.42	4.97	1.12

tivity to VPTBBA. As VCHA does not contain a phenyl ring, the similar selectivities found on both VPTBBA and VCHA suggest that polar ester groups which are involved in the structure of both packing materials play an important role in the retention selectivity for TCDDs on VPTBBA. On silica-based NPE stationary phase, TCDDs having higher dipole moments tended to be retained longer, but this rule could not be applied to VPTBBA. On VPTBBA, 1,4,6,9-TCDD had the smallest k' value, whereas 2,3,7,8-TCDD was retained with the second largest k'. This is very interesting because 2,3,7,8-TCDD, which is reported to have the strongest toxicity [33,34], is a planar TCDD and 1,4,6,9-TCDD may have a staggered structure because of steric repulsion of two pairs of two chlorine atoms and an oxygen atom between the two chlorine atoms (Fig. 11). This means that VPTBBA can recognize the planarity of the TCDDs also. A typical case is the separation of the isomer pair of 1,2,6,7- and 1,2,8,9-TCDDs (Fig. 11). On silica-based NPE stationary phase, these two isomers could be well separated based on the difference in their dipole moments [32]. As 1,2,6,7- and 1,2,8,9-TCDDs have dipole moments of 0.023 and 4.220 D [35], respectively, 1,2,8,9-TCDD is retained longer on the NPE stationary phase. On the other hand, on VPTBBA, these two isomers could not be separated at all, probably because 1,2,8,9-TCDD has more staggered structure than 1,2,6,7-TCDD owing to the two chlorine atoms at the 1- and 9-positions and the selectivity caused by the steric selectivity and dipole moment may offset their selectivities on VPTBBA. Moreover, on VPTBBA, the six TCDDs which have k' values smaller than 1.0 (1,2,3,4-, 1,2,4,6-, 1,2,6,7-, 1,4,6,9-, 1,2,6,9- and 1,3,6,9-) involve at least two chlorine atoms at the 1-,4-,6- or 9-positions, which may decrease their planarity, whereas the five TCDDs with k' larger than 1.2 (1,2,3,7-, 1,2,3,8-, 1,2,7,8-, 1,3,7,8- and 2,3,7,8-) involve only one or no chlorine atom at these positions. These findings also strongly suggest that steric selectivity is one of the most important retention parameters on VPTBBA. A combination of these two major selectivities can determine the separation selectivity on VPTBBA, and therefore the selectivities on the three different stationary phases are not identical, but if the ratios between k' of 1,4,6,9- and 2,3,7,8-TCDDs are compared, it is interesting that VPTBBA has a value of 1.82 whereas ST and VCHA have values of 1.76 and 1.06, respectively. These high steric selectivities found on VPTBBA are consistent with those in the previous sections.

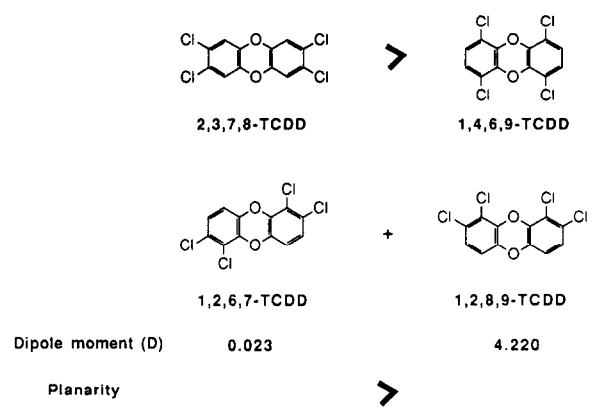

Fig. 11. Retention selectivity of VPTBBA toward TCDDs.

CONCLUSIONS

VPTBBA prepared with ethylene dimethacrylate as cross-linking agent showed a bimodal broad pore size distribution because of the difference in copolymerization reactivity ratio. In a comparison of its chromatographic properties with those of a silica-based stationary phase C_{18}, VPTBBA showed preferential retention toward chlorinated aliphatic compounds with much higher steric selectivity, whereas it has a π-acidic ligand compared with the retention selectivity of a poly(styrene–divinylbenzene) particle. In the separation of TCDDS, VPTBBA retained planar isomers preferentially and dipole–dipole interactions sometimes offset this high steric selectivity, resulting in poor resolution.

In comparison with the chromatographic properties of two other poly(vinyl carboxylate)s, VBA and VCHA, the *tert.*-butyl substituent contributed the hydrophobicity of the particles and also enhanced the steric selectivity. Although the separations of TCDDs are relatively poor on polymer-based separation media, those polymer-

based separation media are effective for the concentration of TCDDs from aqueous mobile phases, because they show much longer retention times than silica-based separation media. Although the quantitative introduction of vinyl *p-tert.*-butylbenzoate could not be achieved, VPTBBA is potentially a good separation medium and absorption medium and its moderate hydrophobicity makes it possible to apply it for the practical concentration of organohalides from aqueous environments.

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