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Polymer-based packing materials for reversed-phase liquid chromatography

Steric selectivity of polymer gels provided by diluents and cross-linking agents in suspension polymerization

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ABSTRACT

The effects of preparation conditions on the pore structures and chromatographic properties of porous polymer gels were studied. The diluents in suspension copolymerization of methyl methacrylate with a divinyl monomer affected the size and volume of micropores as well as those of the macropores. The use of a non-solvent to the polymer such as alkanes and *n*-alkyl alcohols resulted in polymer gels with micropores of smaller size and volume, accompanied by large macropores. Preferential retention of rigid, compact solutes was observed with such polymer gels due to the size-exclusion effect of the micropores. In contrast, better solvation of the polymer with cyclohexanol during polymerization resulted in gels with micropores of larger size and volume, leading to the preferential retention of bulky molecules, while producing macropores of smaller size and volume. Preferential retention of rigid, compact solutes was also observed with gels with higher cross-linking density.

INTRODUCTION

Steric selectivity in reversed-phase liquid chromatography (RPLC) has been observed with various packing materials. Octadecylsilylated silica packing materials prepared from octadecyltrichlorosilane showed preferential retention of planar compounds compared with bulky hydrocarbons [1,2]. Similar results were obtained with silica-based stationary phases with longer alkyl groups compared with those with shorter alkyl chains [3]. Ordered structures of long alkyl chains were found to be responsible for the steric selectivity. In contrast with the flexible alkyl-bonded stationary phase, graphite carbon packing materials possess rigid, planar surfaces, which resulted in the preferential retention of aryl or alkyl compounds with planar structures due to the contribution of dispersion forces and charge-transfer interactions that are strongly influenced by steric complementarity between solutes and the stationary phase [4–6].

Cross-linked polymer gels based on poly(alkyl methacrylate), esterified poly(vinyl alcohol), and polystyrene, were shown to possess common steric selectivity, leading to the preferential retention of rigid, compact compounds compared with bulky, flexible compounds [7–9]. The size-exclusion effect has been observed not only with high-molecular-weight solutes such as polypeptides but also with low-molecular-weight compounds [7–10]. The selec-

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tivity of polymer gels for small molecules was assumed to be provided by the contribution of the microporous structure of polymer gels which gives strength to the gels. The biporous structures, macroporous gels with microporous skeletons, have been substantiated by bimodal pore size distributions [7,9,11,12].

Polymer gel packing materials for high-performance liquid chromatography (HPLC) are commonly prepared by suspension polymerization in water where a polymerization reaction takes place in oil droplets containing a monomer, a cross-linking agent, an initiator and a diluent. The presence of an inert diluent results in the formation of pores through phase separation in the oil droplets during polymerization. The effect of polymerization conditions on the macropore structures has often been studied [10–17]. Easy control of pore size is one of the advantages of polymer packing materials, as shown by the production of particles with extremely large pores [18] and continuous porous rods [19].

A study of the effect of micropore structure on chromatographic properties of styrene-divinylbenzene gels [10] suggests the importance of such a study that can relate the preparation methods of the polymer gels to the pore structures and the chromatographic properties of the products. This paper reports that polymer gels prepared from the same monomer and the cross-linking agent can show considerable difference in steric selectivity depending on the diluent in the gel preparation process. The contribution of the micropore structures determined by the diluents and cross-linking agents provides explanations for the retention mechanisms of polymer gels, which are often difficult to explain on the basis of the hydrophobic interactions that are predominant in RPLC with silica-based packing materials.

EXPERIMENTAL

Preparation of polymer gels

Cross-linked polymer gel beads were prepared by radical suspension copolymerization of methyl methacrylate (MMA) with a divinyl monomer in the presence of a diluent and 2,2′-azobis(2,4-dimethylvaleronitrile) as an initiator [20]. Typically a mixture of MMA (12.5 g), a cross-linking agent (12.5 g), a diluent (25 g) and the initiator (0.25 g) was suspended in a 1% aqueous solution (100 ml) of poly(vinyl alcohol) (degree of polymerization, DP = 2000, Nacalai-Tesque, Kyoto, Japan) by using an ultradisperser (Yamato, Model LK 21, Tokyo, Japan) for 1 min. The feed ratio, monomer/cross-linking agent/diluent (25:25:50, w/w/w), was maintained unless stated otherwise. Polymerization was carried out at 80°C for 10 h without stirring. After polymerization the resulting beads were washed successively with hot water, methanol and acetone, then refluxed in tetrahydrofuran (THF).

The beads were sieved in methanol with a 44-μm sieve. The fraction that passed through the sieve was collected and decanted three times after 15 min of sedimentation to remove fines. The beads were packed into a stainless-steel tube (100 mm × 4.6 mm I.D.) with a mixture of cyclohexanol and 2-propanol, or 2-propanol and methanol as a slurry medium.

Materials

The monomer and all the cross-linking agents, ethylene dimethacrylate (EDM), pentaerythritol tetraacrylate, butane-1,4-diol dimethacrylate, cyclohexane-1,4-diol dimethacrylate (*cis* and *trans* mixture) and divinylbenzene, were either purchased or prepared by standard procedures. The following compounds were used to illustrate the steric selectivity of each polymer gel in RPLC: (**1**) pentane, (**2**) hexane, (**3**) heptane, (**4**) octane, (**5**) nonane, (**6**) decane, (**7**) cyclohexane, (**8**) adamantane, (**9**) *trans*-decalin, (**10**) naphthalene, (**11**) anthracene, (**12**) pyrene, (**13**) phenanthrene, (**14**) diphenylmethane, (**15**) *o*-terphenyl, (**16**) triphenylene, (**17**) triptycene, (**18**) triphenylmethane, (**19**) fluorene, (**20**) benzene, (**21**) toluene, (**22**) ethylbenzene, (**23**) propylbenzene, (**24**) butylbenzene, (**25**) amylbenzene. The structures of (**8**) adamantane, (**9**) *trans*-decalin, (**11**) anthracene, (**12**) pyrene, (**15**) *o*-terphenyl, (**16**) triphenylene, and (**17**) triptycene are shown in Fig. 1. The silica C_{18} material is similar to that used in a previous study [9].

Equipment

The HPLC system consisted of an 880 PU pump (Jasco, Tokyo, Japan), a Model 440 UV detector and an R401 refractive index detector (Waters, Milford, MA, USA) and a Model 7000A data processor (System Instruments, Tokyo, Japan). The col-

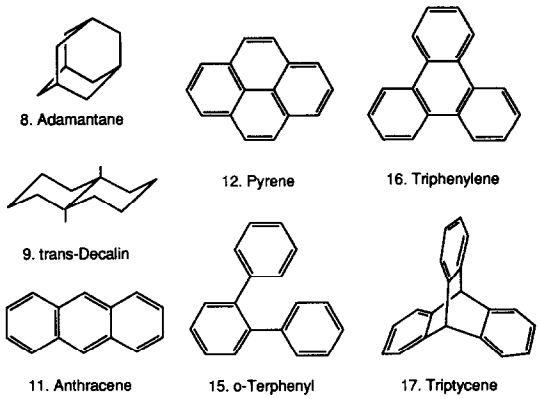

Fig. 1. Structures of hydrocarbons used to illustrate the steric selectivity of polymer gels.

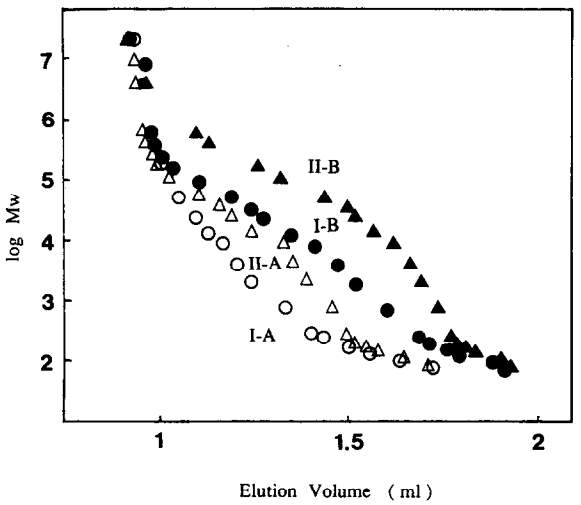

Fig. 2. Molecular weight–elution volume plots for the polymer gels prepared in cyclohexanol (I-A and I-B) and 2-octanol (II-A and II-B). Mobile phase: THF. Column size: 150 × 4.6 mm I.D. Solute: polystyrene and alkylbenzenes. ○ = I-A; ● = I-B; △ = II-A; ▲ = II-B. See Table I for gel identification.

umn temperature was maintained at 30°C with a water-bath.

RESULTS AND DISCUSSION

Characterization by size-exclusion chromatography

The pore volume and pore size of porous polymer gels, with respect to meso- and macropores, are known to be affected by the properties of diluents used for the suspension polymerization [11–17]. Series of products with various pore sizes are available for size exclusion chromatography. The effect of diluents on micropore structures was examined to explain the steric selectivity of polymer gels in RPLC.

Four types of polymer gels were prepared by copolymerization of MMA with EDM using two diluents, cyclohexanol and 2-octanol, at two monomer concentrations. The resulting gels showed no appreciable swelling in methanol or in THF.

Fig. 2 shows the results of size exclusion chromatography of polystyrene standards in THF with these polymer gels. The molecular weight–elution volume curves were bimodal in all instances, show-

TABLE I

EXCLUSION LIMITS AND PORE VOLUMES OF POLYMER GELS

Column size: 150 × 4.6 mm I.D. Mobile phase: THF.

Polymer gel No.	Diluent (monomer/diluent ratio, w/w)	Exclusion limit (log MW)[a]	Total pore volume (ml) V_p[b]	Micropore volume (ml) V_a[c]	V_b[d]
I-A	cyclohexanol (5:2)[e]	5.4	0.89	0.23	0.17
I-B	cyclohexanol (5:5)[e]	5.6	0.97	0.15	0.16
II-A	2-Octanol (5:2)[e]	5.5	0.91	0.17	0.09
II-B	2-Octanol (5:5)[e]	6.2	1.14	0.12	0.08

[a] Log (molecular weight) of polystyrene.
[b] V_p: elution volume (EV) of polystyrene standard (molecular weight > 1 000 000) was subtracted from that of benzene.
[c] V_a: EV (benzene) − EV (hexylbenzene).
[d] V_b: EV (hexylbenzene) − EV (polystyrene, molecular weight 760)
[e] (MMA + EDM)/diluent ratio in feed.

ing the presence of macropores and micropores. (In the later section of this paper, pores larger than those usually referred to as micropores, showing selective permeation for polystyrenes of molecular weight greater than 1000, are referred to as macropores.) The results indicate that the increase in the diluent content in the suspension feed resulted in the greater total pore volume and the larger macropores, as shown in Fig. 2 and in Table I.

The effect of the diluent type on gel structure is clearly observed in the comparison between I-B and II-A. Macropores are more easily formed in the presence of 2-octanol. I-B and II-A possess similar exclusion limits, or the size of macropores. These gels, however, possess considerable differences in pore volume in the macropore and micropore region. Fig. 2 and Table I indicate that the gels possessing the greater macropore volume and the greater exclusion limit generally possess smaller pore volume in the micropore region. As shown in Table I, I-B possesses the greater pore volumes in the micropore ranges, V_a and V_b, corresponding to the difference in elution volumes of benzene and hexylbenzene and that of hexylbenzene and polystyrene (molecular weight 760), respectively, than II-A. Nitrogen adsorption measurement showed two pore-volume maxima at pore sizes of 1.7 and 17 nm for I-B, and at 1.7 and 12 nm for II-A.

Selectivity towards low-molecular-weight solutes under RPLC conditions

In a previous study, the bimodal pore size distribution, particularly the presence of micropores about the size of solute molecules, was thought to be responsible for the unique selectivity of polymer gels which appeared as the preferential retention of rigid, compact solutes in RPLC [7,9]. Such steric selectivity may also be provided by the lightly cross-linked polymer chains on the gel surface [21].

Fig. 3a compares selectivities between the polymer gel I-B and silica C_{18}. The polymer gel showed the preferential retention of the rigid solutes. When the log k' values on gel II-A were plotted against those on silica C_{18} (Fig. 3b), considerable differences in selectivity were found from that in Fig. 3a. As the measurements were carried out in the same mobile phase, the selectivity difference between I-B and II-A, shown in Fig. 3c, must be explained by the difference in gel structure. Steric factors are responsible for the difference in selectivity, because the selectivity difference was also observed with the saturated compounds. The previous study showed the substantial differences in steric selectivity between the polymer gels provided by several manufacturers together with the general tendency of preferential retention of rigid, compact solutes compared with silica-based phases [9].

The steric selectivity, or the separation factor (k' value of a bulky molecule divided by that of a compact molecule), for several pairs of hydrocarbons with different rigidities and compactness is shown in Table II. The four packing materials prepared from the same monomers with the same feed ratios showed very similar hydrophobic selectivities in terms of the increase in retention caused by one methylene group, $\alpha(CH_2)$. In spite of the consid-

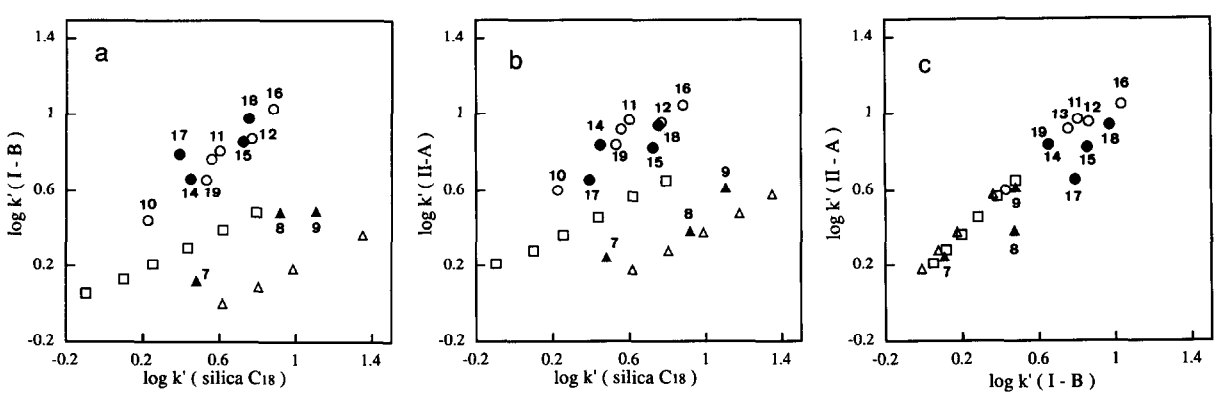

Fig. 3. Comparison of selectivity between polymer gels and octadecylsilylated silica gel in methanol–water (80:20). (a) Log k' values on I-B *versus* log k' values on silica C_{18}. (b) Log k' values on II-A *versus* log k' values on silica C_{18}. (c) Log k' values on I-B *versus* log k' values on II-A. Solutes as numbered, except alkanes (△, C_nH_{2n+2}, n = 6–10) and alkylbenzenes (□, $C_6H_5C_nH_{2n+1}$, n = 0–5).

TABLE II

EFFECT OF DILUENTS ON THE SELECTIVITY OF POLYMER GELS

Mobile phase: 80% methanol.

Solute	α^a (k')[b]			
	I-A[c] (in cyclohexanol)	I-B[c] (in cyclohexanol)	II-A[c] (in 2-octanol)	II-B[c] (in 2-octanol)
$\alpha(CH_2)$[d] (No. 6)	1.24 (4.83)	1.25 (2.38)	1.24 (3.73)	1.24 (2.20)
α[**8**]/[**9**] (No. 9)	0.97 (6.67)	0.98 (3.07)	0.58 (4.11)	0.52 (2.38)
α[**17**]/[**11**] (No. 11)	1.11 (12.8)	0.97 (6.45)	0.49 (9.24)	0.45 (5.59)
α[**12**]/[**11**]	1.20	1.15	0.96	0.89
α[**15**]/[**16**] (No. 16)	0.66 (22.7)	0.67 (10.8)	0.60 (11.2)	0.61 (5.74)
V_a[e]	0.23	0.15	0.17	0.12
V_b[e]	0.17	0.16	0.09	0.08

[a] Separation factor beween the two compounds shown on the left.
[b] k' value of the compound is given in parentheses. Identification: No. 6 = decane; No. 8 = adamantane; No. 9 = *trans*-decalin; No. 11 = anthracene; No. 12 = pyrene; No. 15 = *o*-terphenyl; No. 16 = triphenylene; No. 17 = triptycene.
[c] See Table I for other preparation conditions.
[d] k'(amylbenzene)/k'(butylbenzene).
[e] See Table I for V_a and V_b. V_a: EV(benzene) − EV(hexylbenzene); V_b: EV(hexylbenzene) − EV(polystyrene, molecular weight 760) in THF.

erable difference in the size of macropores and the pore volumes in the macro- and micropore regions, the polymer gels prepared in the same diluent, I-A and I-B, and also II-A and II-B, showed very similar steric selectivity. The gels prepared in cyclohexanol consistently gave a greater preference towards bulky solutes. The greatest differences were seen for the combinations of decalin–adamantane and anthracene–triptycene, each of which possesses a considerable difference in molecular planarity and bulk.

The results shown in Table II indicate that the pore volume in a smaller micropore size range, V_a, determines the retention (k' values) of the compact solutes, whereas the retention of the bulky molecules reflects the pore volume in a larger micropore size range, V_b. Thus the steric selectivity between the planar, compact molecules and the bulky molecules can be attributed to a size-exclusion effect of micropores of polymer gels determined by the type, not the content, of the diluent used in suspension polymerization.

The size of micropores is determined by the solvation of polymer chains with the diluent in the polymerization process. Poorer solvents to the growing polymer chain result in earlier polymer precipitation, or earlier phase separation. In this instance the precipitating polymers are relatively free from the diluent due to the lack of solvation. The resulting polymer gels possess the larger macropores and smaller micropores [14], which in turn is related to the small retention of bulky solutes compared with the compact solutes in RPLC.

In contrast, when the diluent is a slightly better solvent to the polymer chain, polymerization proceeds more homogeneously, resulting in later phase separation. Precipitating polymers contain more diluent molecules, resulting in the larger micropores, whereas the size of macropores are limited [14]. The resulting gels show a preference toward bulky molecules. The explanation is compatible with the observation that the MMA homopolymer (molecular weight 20 000) is appreciably soluble in hot cyclohexanol, but not in 2-octanol. Little difference in solubility is seen either in the solubility parameters [22,23] or in experimentally obtained solubility at room temperature.

Fig. 4 shows the chromatograms obtained with gels I-B and II-A. The two gels, prepared from the same combination of a monomer and a cross-linking agent, showed a considerable selectivity difference. The largest effect was observed with bulky

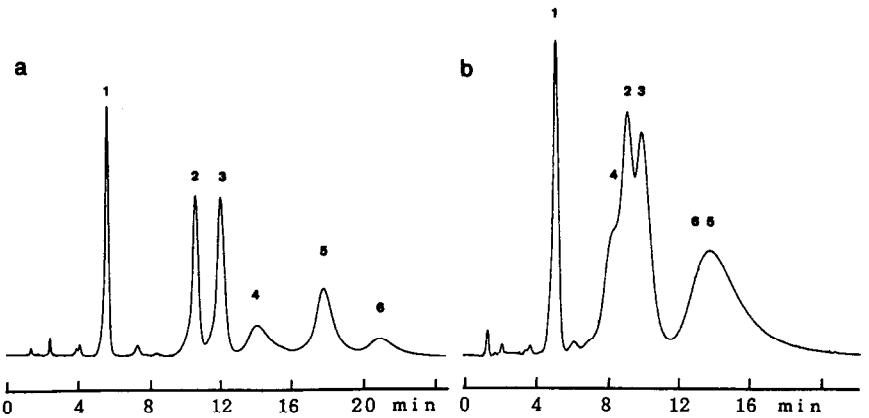

Fig. 4. Elution of some aromatic compounds on polymer gels. Stationary phase: (a) I-B and (b) II-A. Mobile phase: acetonitrile–water (60:40). Flow-rate: 0.8 ml/min. Solutes: **1** = benzene; **2** = butylbenzene; **3** = diphenylmethane; **4** = triptycene; **5** = pyrene; **6** = triphenylmethane.

triptycene (peak 4) and triphenylmethane (peak 6). Diffuse reflectance Fourier transform infrared (FTIR) spectra showed no difference between the two polymer gels prepared in the two diluents, as expected. These results suggest that the chromatographic examination can be used for characterizing or differentiating polymer gels with similar compositions, even if FTIR measurements are not useful in differentiating the preparation method.

The size-exclusion effect can be seen not only for three-dimensionally bulky molecules but also for planar polynuclear aromatic compounds such as pyrene and triphenylene with gels prepared in the presence of considerable concentrations of non-solvents. The effect, however, was not seen with anthracene or naphthalene, as shown in the plot in Fig. 3c, where pyrene and triphenylene showed a slight deviation from the general tendency found for the other more compact molecules. Although the steric selectivity inherent to polymer packing materials has been attributed to the size-exclusion effect based on micropores, the possible contribution of lightly cross-linked polymer chains on the gel surface [21] needs to be examined.

Effect of other diluents

Several other diluents and mixtures were examined with respect to their ability of forming macro- and micropores. Isooctane, a non-solvent of the polymer, resulted in large macropores and small amount of micropores when used as a mixture with cyclohexanol. Similar results were reported in the polymerization of other monomers [12,14,16]. As indicated in Fig. 5 and Table III, the polymer gel, III-B, prepared in a cyclohexanol–isooctane (60:40) mixture showed a similar selectivity to those prepared in 2-octanol or in 1-hexanol.

The diluent, cyclohexanol–isooctane (40:60), produced gels with no macropores. Similar results were obtained with decalin. The polymer gel (V) prepared in butyl acetate, possesses a similar pore structure to the gel III-A prepared in a cyclohexanol–isooctane (80:20) mixture, showing an intermediate steric selectivity. Good solvents to the polymer such as ethylbenzene, xylene and toluene produced gels with only micropores. These gels showed prolonged retention times for solutes with compact structures which can enter the micropores, whereas bulky solutes such as triptycene were excluded from the pores and eluted very early in the chromatogram, as shown in Fig. 5b. These results indicate that the pore structures and the retention selectivities in RPLC of MMA–EDM gels can be controlled by the choice of diluents in suspension polymerization.

Effect of cross-linking agents

Fig. 6 illustrates the effect of the structure of cross-linking agents on the steric selectivity of polymer gels. In each part of the figure a straight line

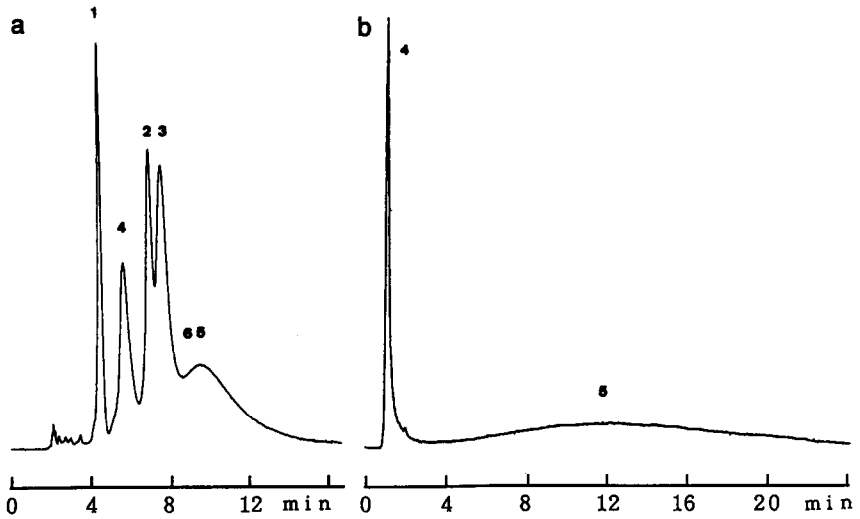

Fig. 5. Elution of some aromatic compounds on polymer gels. Stationary phase and mobile phase: (a) III-B [diluent: cyclohexanol–isooctane (60:40), acetonitrile–water (60:40)], (b) VI [diluent: xylene), methanol–water (80:20)]. Flow-rate: 0.8 ml/min. Solutes as in Fig. 4.

with a slope of unity through the origin is shown as a broken line. The gels prepared from the dimethacrylate ester of butane-1,4-diol and cyclohexane-1,4-diol (*cis* and *trans* mixture) generally resulted in a greater retention than that prepared from EDM, presumably due to the greater hydrophobic properties of the cross-linking agent.

The gels containing cyclohexane moieties

TABLE III

EFFECT OF DILUENTS ON THE SELECTIVITY OF POLYMER GELS

Mobile phase: 80% methanol.

Solute	α^a (k')^b			
	III-A^c (in cyclohexanol–isooctane)	III-B^d (in cyclohexanol–isooctane)	IV-A (in 1-hexanol)	V (in butyl acetate)
$\alpha(CH_2)^e$ (No. 6)	1.25 (2.58)	1.24 (2.08)	1.21 (1.84)	1.23 (2.29)
α**[8]**/**[9]** (No. 9)	0.87 (3.38)	0.54 (2.60)	0.66 (1.97)	0.71 (2.75)
α**[17]**/**[11]** (No. 11)	0.74 (6.83)	0.41 (5.64)	0.55 (4.80)	0.71 (6.13)
α**[12]**/**[11]**	1.09	0.95	0.96	1.08
α**[15]**/**[16]** (No. 16)	0.66 (10.2)	0.59 (5.91)	0.61 (6.01)	0.61 (9.17)
V_a[f]	0.15	0.11	0.15	0.14
V_b[f]	0.11	0.06	0.09	0.08

[a] Separation factor beween the two compounds shown on the left.

[b] k' value of the compound is given in parentheses. Identification: No. 6 = decane; No. 8 = adamantane; No. 9 = *trans*-decalin; No. 11 = anthracene; No. 12 = pyrene; No. 15 = *o*-terphenyl; No. 16 = triphenylene; No. 17 = triptycene.

[c] Prepared in a mixture cyclohexanol–isooctane (80:20).

[d] Prepared in a mixture cyclohexanol–isooctane (60:40).

[e] k'(amylbenzene)/k'(butylbenzene).

[f] See Table I for V_a and V_b. V_a: EV(benzene) − EV(hexylbenzene), V_b: EV(hexylbenzene) − EV(polystyrene, molecular weight 760) in THF.

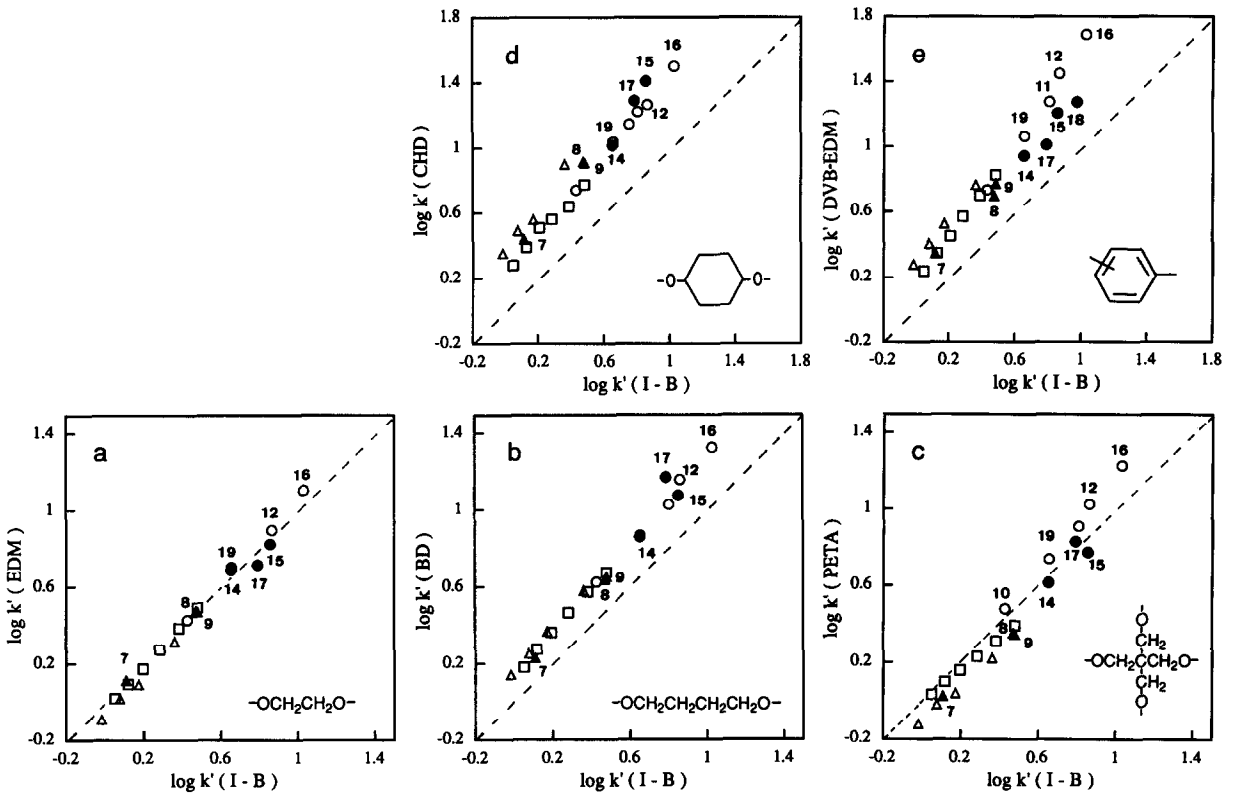

Fig. 6. Effect of cross-linking agents on steric selectivity of polymer gels. Monomer and cross-linking agent: (a) EDM 100%; (b) MMA–butane-1,4-diol dimethacrylate (BD) (40:60, w/w); (c) MMA– pentaerythritol tetraacrylate (PETA) (50:50, w/w); (d) MMA–cyclohexane-1,4-diol dimethacrylate (CHD) (45:55, w/w); (e) MMA–divinylbenzene–EDM (EDM–DVB) (50:25:25, w/w/w). Solutes as in Fig. 3.

showed preferential retention of bulky, non-planar solutes compared with I-B. The results can be explained on the basis of the lower cross-linking density or larger micropores in this gel, and the non-planarity of bridging moieties. The small retention of planar solutes on cyclohexane-bonded silica [24] and the small retention of alicyclic compounds on graphite carbon packing materials [6] are an indication of the less favourable interaction between the planar structure of the polycyclic aromatic moieties and the non-planar structure of cyclohexane rings.

Divinylbenzene resulted in a gel showing a preferential retention of planar aromatic over bulky aromatic compounds, together with a greater hydrophobic retention. Pentaerythritol tetraacrylate gave a gel with a preference towards the more rigid, compact solutes. The greater cross-linking density of these gels, resulting in the smaller micropores, can account for the greater size-exclusion effect.

CONCLUSIONS

The steric selectivity of polymer gels, or the preferential retention of rigid, compact molecules in RPLC, was shown to be a size-exclusion effect provided by the micropore structure. The effect of diluents in suspension polymerization of MMA on pore size and volume was observed in a micropore region and in a macropore region. The use of non-solvents, alkanes and n-alkyl alcohols, resulted in the smaller micropore structures leading to the greater size-exclusion effects, whereas these solvents produced the larger macropores. The pore size control of poly-MMA gels by using cyclohexanol in combination with a non-solvent will allow the con-

trol of selectivity in RPLC. The feasibility of pore size control for small molecules, shown in this study, as well as for biological macromolecules as reported previously [18,19], is an advantage of polymer-based packing materials for RPLC.

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