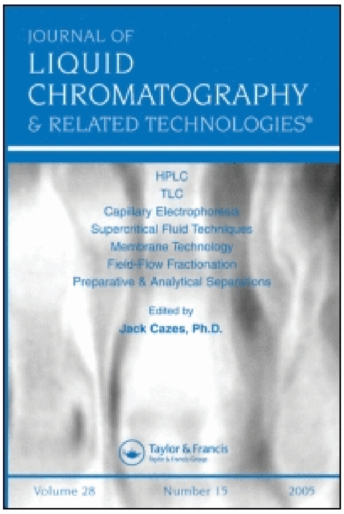

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POLYMER RETENTION MECHANISM IN GPC ON ACTIVE GELS. II. LOW MOLECULAR WEIGHT POLYSTYRENE

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ABSTRACT

The elution behaviour of low molecular weight polystyrene (PS) down to the monomer on spherosil gel in several eluents has been studied. In the medium range of molecular weights the elution behaviour is similar to that followed by high molecular weight PS, the differences in elution volumes among different eluents increasing monotonically with decreasing molecular weight and partition rather than adsorption probably being responsible for the shifts in retention volumes. However, at the total permeation limit, the situation is alike to that found in liquid-solid chromatography, the elution volumes of solutes with molecular sizes very close to that of styrene being determined by solvent strength ($\varepsilon°$) and solute solubility (δ) parameters. Hydrogen bonding seems to be the main contribution to substrate-solute interactions in this case.

INTRODUCTION

In gel permeation chromatography (GPC) on active supports such as polar inorganic gels, the hydrodynamic volume curves for polystyrene (PS) in poor solvents shift in some cases to lower (*1,2*), in other to higher (*3,4*) retention volumes in comparison with a good solvent. The universal calibration concept (*5*) , hydrodynamic volume vs. retention volume, is useless because adsorption and partition phenomena due to the polarity of support start playing a role in the separation mechanism (*4*, *6-9*).

In the previous paper of this series (*9*), the elution behaviour of PS in the molecular weight range from 2000 up to 660000 on spherosil XOA 200 in twenty one eluent systems was studied. Changes in elution curves were explained in terms of polymer-gel (p-g), solvent-gel (s-g) and polymer-solvent (p-s) interactions, as defined by the eluent strength ($\varepsilon°$) and the α exponent of the Mark-Howink (MH) equation. The application of a network-limited partition and a network-limited adsorption mechanism (*10-11*) to the elution experimental results allowed the evaluation of relative distribution coefficients f_i, defined as $f_i = K_{p_i}/K_{p_0}$, being K_{p_i} and K_{p_0} the respective distribution coefficients in the eluent i and in the standard eluent. f values showed a joint dependence on $\varepsilon°$ and α. At low α and at high $\varepsilon°$, partition rather than adsorption seems to be the predominant effect governing f values. When $\varepsilon°$ decreases, increasing adsorption effects must be added to the partition ones.

α exponents of the MH equation decay to the value $\alpha = 0.50$ with decreasing molecular weight of polymers. Therefore, at molecular weights low enough, the hydrodynamic sizes of polymer molecules become practically constant irrespective of the solvent and the task of separating steric exclusion primary contributions from secondary partition and/or adsorption effects must be eased. Because of that and in order to get a deeper knowledge on those secondary effects, the elution behaviour of low molecular weight PS down to the monomer in different eluents is shown in this paper.

EXPERIMENTAL

The experiments were run on a Waters Assoc. ALC/GPC 202 liquid chromatograph. A Pharmacia SR 25 column (45 × 2.5 cm I.D.) packed with a mixture (25 + 25 g) of sherosil XOA 400 + spherosil XOA 200 both of high granularity was used. The rest of the experimental conditions as well as the detailed description of the equipment used have been already published (9).

Sixteen PS samples covering the molecular weight range from 450 up to 24700 have been studied. The samples with the lowest molecular weights, namely, those with nominal molecular weights 450, 750, 980 and 1100, as determined by vapour pressure osmometry, were kindly supplied by Dr. L.M. León of the Physical Chemistry Department of Bilbao University. They were cationically prepared in dichlormethane at 0°C using as an initiator perchloric acid and very low monomer/initiator ratios (*12*). Their $(M_w/M_n) \simeq 1.2$. The remaining samples with narrow molecular weight distributions, $(M_w/M_n) < 1.13$ in all cases, were provided by Pressure Chemical Co., Centre des Recherches sur les Macromolecules (Strasbourg) and Waters Assoc.

Intrinsic viscosities were measured with a conventional modified Ubbelohde viscometer.

RESULTS AND DISCUSSION

The elution behaviour of a given solute is expressed by the relationship between the "size" of the solute in solution and its retention volume. Depending on the physical magnitude used to define the molecular size, different elution curves will be obtained. The newest approach is based on the concept that the elution volume should be sensitive to the effective hydrodynamic volume of the polymeric chain in solution leading to the concept of universal calibration (5). Hydrodynamic volumes may be evaluated through the unperturbed mean radius of gyration, $\langle s^2\rangle_0^{1/2}$,

$$\langle s^2\rangle_0^{3/2} = |\eta| M \; / \; 6^{3/2} \, \Phi_0 \qquad (1)$$

or even better, in order to take into account excluded volume effect, ε, through the corresponding perturbed dimension

$$\langle s^2\rangle^{3/2} = |\eta| M \; / \; 6^{3/2} \, \Phi(\varepsilon) \qquad (2)$$

or through the hydrodynamic radius, R,

$$R^3 = |\eta|\ M\ /\ \frac{1}{3}\pi\ N_A\ 10^{-25} \qquad (3)$$

where $|\eta|$, the limiting viscosity number, is expressed in $dl.g^{-1}$, M, molecular weight, in $g.mol^{-1}$, N_A is the Avogadro's number and the dimensions of $<s^2>^{1/2}$ and R are Å. Anyway, the product $|\eta|M$ is a measure of the hydrodynamic volume and it is directly related to the eluted volume

$$\log(|\eta|M) = f(V_R) \qquad (4)$$

the above function describing the overall elution behaviour of a polymer in a given set of columns in a given or any solvent.

Two points, however, deserve some comments prior to describe the elution behaviour followed by the low molecular weight PSs, studied in this paper. The first one is directly related with the validity of eqs. (1) , (2) and (3) to describe properly molecular sizes of low molecular weight solutes. When the chain is short enough it has to be regarded as a partial draining body with respect to solvent, eq. (3) not being valid, as well as eqs. (1) and (2) unless Φ_0 is considered as a variable depending on chain length (*13*). Several theories have been developed to predict that variation (*14-17*), most of them following the Rouse-Zimm formalism for the dynamics of the chain, and unfortunately most of them not being able to reproduce experimental data.

The second point is related with $|\eta|$ values of low molecular weight samples. In turn, this second aspect must be looked from both an experimental and a theoretical points of view. The purely experimental one is related with the uncertainty of $|\eta|$ values because flow times of the polymeric dilute solutions and of the pure solvent are very close. This uncertainty can disappear by improving the experimental technique. However, when the solute molecular chain is short, solute and solvent molecules are of comparable size and the influence of the solvent molecular volume can not be neglected. As pointed out by Horta et al. (*18*) the contribution of the solvent $|\eta|_s$ must be added to the experimental $|\eta|$ to calculate a corrected value, $|\eta|_c$, which presumably reflects the limiting viscosity number of the solute in a solvent composed of molecules of zero volume. The correction method used by Horta et al. assumes that $|\eta|_s$ is proportional to the hydrodynamic volume of the solvent molecules and it is similar to the one proposed by Rossi and Perico (*19*), which take into consideration chain thickness. In any case, it is significant and it must be stressed that the corrected $|\eta|_c$ values obtained for n-alkanes (C_nH_{2n+2} , $5 < n < 40$) are similar irrespective of the solvent (benzene and carbon tetrachloride) (*18*) and this seems also to be the case for $|\eta|_c$ values of short hydrocarbons in xylene and in n,heptane (*19*).

The same conclusion can also be reached from a slightly different approach. When working with low molecular weight polymers α values of the MH eq. approach 0.50 in all the solvents and the differences in $|\eta|$ values are negligible between different solvents.

In this paper we compare the elution behaviours of low molecular weights PSs in different eluents. We have used M instead $M|\eta|$ as the dimension defining molecular size, because the difficulties, described above, dealing with the calculation of the hydrodynamic dimensions and with the appropriate determination of $|\eta|$. Moreover, given that $|\eta|$ values become practically constant irrespective of the solvents, the differences in $\log(M|\eta|)$ for a given M in different eluents are negligible. This effect is clearly shown in table 1, in which the differences $(\log(M|\eta|)_{Eluent} - \log(M|\eta|)_{Benzene})$ are given for different molecular weight samples. Benzene is taken as the reference solvent because it is the richest eluent used from a thermodynamic point of view and therefore in it the highest $|\eta|$ values are obtained , being also the differences in $\log(M|\eta|)$ with respect to it the largest ones. The values enclosed in the table are those corresponding to the two highest molecular weight samples used in this study, namely samples P15 and P16, and to

TABLE 1

Differences between the Hydrodynamic Sizes Logarithms of PSs in several Eluents and in Benzene, expressed as $\log(M|\eta|)_{\mathrm{Eluent}} - \log(M|\eta|)_{\mathrm{Benzene}}$

Eluent (Vol/Vol)	PSX[a]	PS8[a]	PS10[a]	PS15[a]	PS16(a)
Benzene-Methanol (84/16)	0.000	-0.001	-0.001	-0.026	-0.026
Benzene-Methanol (75/25)	-0.021	-0.030	-0.020	-0.092	-0.094
Benzene-n,Heptane (92/8)	0.000	+0.009	+0.020	-0.065	-0.067
Tetrahydrofuran	-0.007	-0.007	-0.002	-0.031	-0.033
Butanone (MEK)	-0.010	-0.010	-0.009	-0.092	-0.094
MEK-n,Heptane (50/50)	-0.030	-0.040	-0.040	-0.182	-0.202

[a] PSX : $|\eta| = 0.0388$, $\overline{M}_n = 2000$; PS8 : $|\eta| = 0.0476$, $\overline{M}_n = 2900$; PS10: $|\eta| = 0.0559$, $\overline{M}_n = 4000$; PS15: $|\eta| = 0.158$, $M_p = 21000$; PS16: $|\eta| = 0.175$, $M_p = 24700$. $|\eta|$s in benzene at 25.0°C in $\mathrm{ml.g^{-1}}$.

the samples PSX, PS8 and PS10 with intermediate molecular weights and close to the limit of the non-draining behaviour. The nominal molecular weights of the above samples as well as their limiting viscosity indexes in benzene at 25.0°C are also gathered as a footnote in table 1. These $|\eta|$ values allow, together with the differences in $\log(M|\eta|)$, the calculation, if necessary, of the $|\eta|$ values in the remaining solvents.

As it must be expected, table 1 results show that $\log(M|\eta|)$ values in different eluents approach to each other with decreasing molecular weights, hydrodynamic sizes becoming constant irrespective of the solvent at the limit of the non-draining behaviour.

Figure 1 displays the elution behaviour of low molecular weight PSs down to the monomer in tetrahydrofuran (THF) and

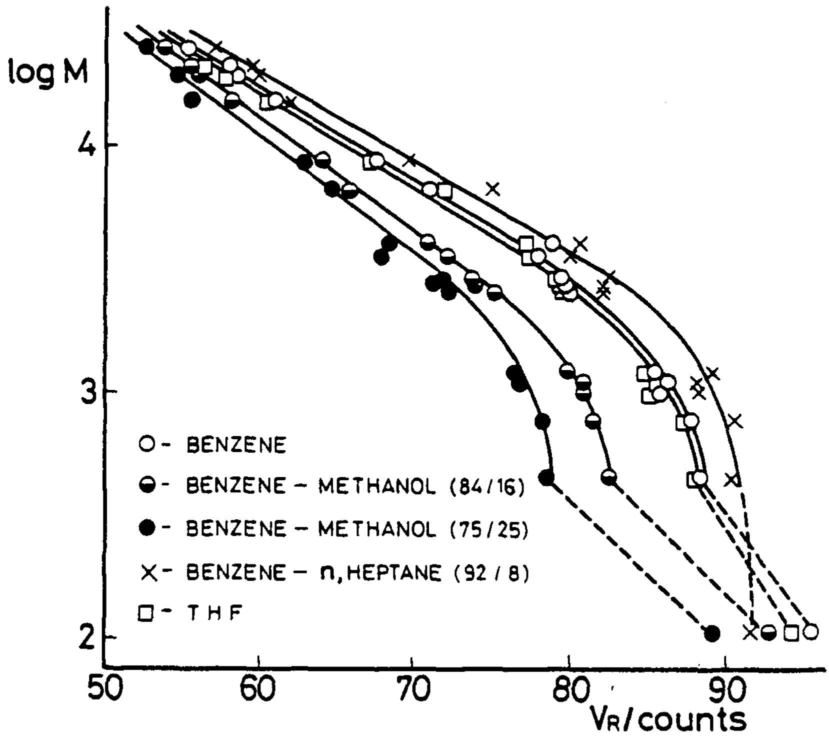

FIGURE 1 .- Elution curves of low molecular weight PS and monomer on spherosil in THF and in benzene and benzene-based mixtures . 1 count = 0.97 ml.

benzene-based mixtures. In figure 2 butanone (MEK)-based mixtures are the eluents. The retention volumes of the dimer of the α,methyl styrene and of ethyl benzene, the model compound of the PS units, have also been enclosed in this last figure. Experimental results of both figures may be summarized by the following points:

a) Elution behaviour of low molecular weight PS is similar in a qualitative way to that followed by its parent high molecular weight compound as a comparison between actual figures 1 and 2 and figure 1 in the previous paper (9) indicates:

- Elution curves in benzene and in THF are very close.

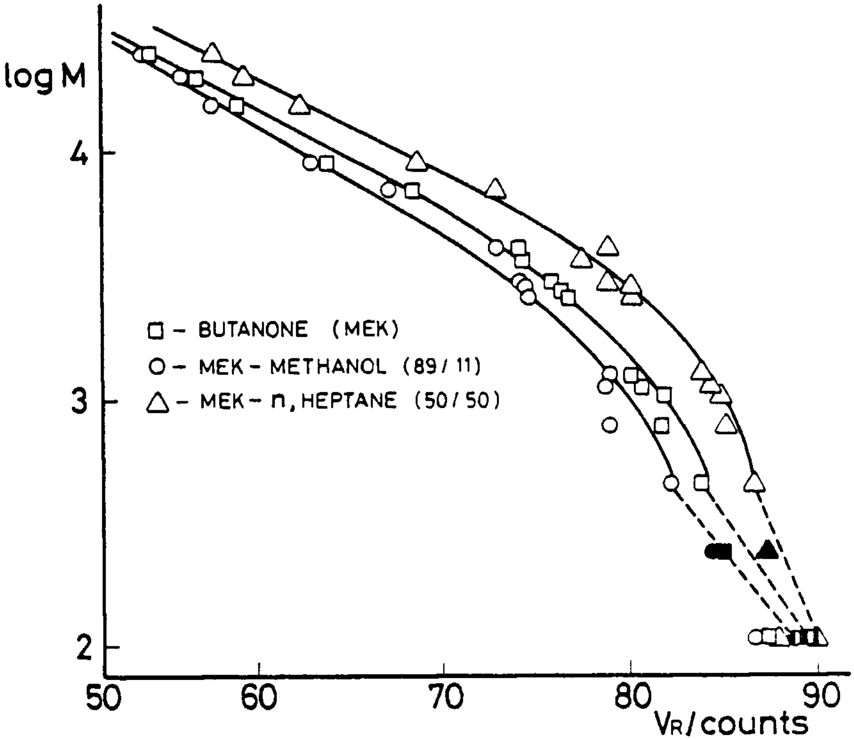

FIGURE 2 .- Elution curves of low molecular weight PS and its monomeric model unit (unfilled points), α,methyl styrene dimer (filled points) and styrene (half filled points) on spherosil in butanone and butanone-based mixtures. 1 count = 0.97 ml.

- n,heptane mixtures deviate to larger elution volumes than the above standard eluents.
- Methanol mixtures, on the contrary, deviate to smaller retention volumes, and no mutual crossing of calibration curves in benzene and its methanol mixtures takes places in the region ol low molecular weights, against the suggestions of Bakos et al. (7).

b) In mixtures deviating to the left, the magnitude of the deviation increases with decreasing molecular weight, whereas in those going to the right it seems that this trend is only followed at the highest molecular weights; at lower molecular weights the differences in elution volumes remain constant (benzene-n,heptane mixture) or even decrease (butanone-n,heptane mixture).

c) Elution volumes of the monomeric model compound and of the α,methyl styrene dimer seem to fit to the elution curves followed by polymer molecules as it is illustrated in figure 2. This is not the case with monomer elution volumes; they do not fit in any case to the elution behaviour of polymer molecules, except in the benzene-n,heptane (92/8) eluent. To illustrate this effect, dotted lines have been drawn between the lowest molecular weight polymer molecule ($\overline{M}_n = 450$) and the monomer.

The conclusions arrived to in our previous paper (9) when studying high molecular weights PSs must be recalled in order to understand the elution behaviour of the low molecular weight samples. The application of a network-limited partition and a network-limited adsorption mechanism to the elution results of high molecular weight PSs seems to indicate that the effective radius of the gel pores is a joint function of solvent strength (ε°) and thermodynamic solvent goodness (α). This fact is probably due to the formation of a layer of a "quasistationary" phase of eluent interacting with substrate (3). In those containing methanol eluents and therefore with high ε° values, a thick quasistationary layer of eluent is formed. The solute will then display its affinity for a mobile and a liquid stationary phases, both phases probably differing in chemical composition (7) . Of course, it must be expected that the stationary phase should be richer in methanol than the mobile one. But the higher the methanol content the poorer thermodynamically is the mixture for the polymer and the weaker the polymer-solvent interactions are. The partition of the polymer between the mobile and the stationary phase would take place in the sense of polymer prefering the mobile phase. Low elution volumes and relative distribution coefficients lower than unity ($f<1.0$) are then obtained. Moreover, being the polymer concentration in the stationary phase very low, the probable adsorption effects by substrate must be very weak. Partition then will be mainly responsible of the shifts towards lower retention volumes occuring with increasing methanol content in the eluent.

On the other hand, in those containing n,heptane systems, the quasistationary phase must be richer in good solvent than the mobile one, the polymer prefering then the former phase and therefore higher retention volumes are obtained. Moreover, being high in these eluents the polymer concentration in the stationary phase, polymer molecules can approach the gel and probable adsorption of polymer by the substrate may start to play a role. In those systems, besides partition, adsorption may also be responsible for the $f>1.0$ obtained values.

In the range of high molecular weights α remains constant and relative distribution coefficients (f) will be molecular weight independent. Differences in elution volumes among different eluents will monotonically increase with decreasing molecular weight, due to the different slopes of the $\log(M|\eta|)$ vs. V_R straight lines. This overall behaviour describing the previous findings for high molecular weight PSs (*9*) is also followed by the highest molecular weight samples of the present study as it is clearly shown in figures 1 and 2.

However, with decreasing molecular weight α starts also to decrease and therefore the differences in thermodynamic quality between eluent in the stationary phase and eluent in the mobile phase will be smaller and as a consequence relative distribution coefficients will move towards the unity in all the eluents. Moreover, in those systems with $f>1.0$, in which adsorption started to play a role, the f shifts towards the unity with decreasing molecular weight will be steeper because the adsorption contributions to f values will also diminish, since numerous studies indicate (*20*) that the adsorption of polymers decreases with molecular weight and as Dubin et al. have pointed out (*8*) site interactions between polymer and substrate can exhibit cooperative neighbouring effects increasing with molecular weight. This could explain the apparent shortening of differences in elution volumes between n,heptane mixtures and the reference systems occuring at the lowest molecular weight region.

Finally, at the total permeation limit, the differences in elution volumes of the monomeric solutes among different eluents must be looked for differences in solute-gel and solvent-gel interactions. The situation is similar to that displayed in liquid-solid chromatography. Elution volumes will be,in general, a function of solvent strength and solute polarity. The unsaturated character of the styrene monomer must increase its affinity for surface silanol groups with respect to that displayed by the model polymeric unit (ethyl benzene). As a result higher retention volumes of the monomer must be expected and figures 1 and 2 put it in evidence in all the studied eluents. This effect is better shown in table 2, in which the elution volumes of several solutes having similar molecular weights but different polarities are shown in some eluents. The solutes in table 2 have been arranged in order of increasing polarity, as defined by their δ solubility parameters (see table 3) and, as it must be expected, their elution volumes in a given eluent are also arranged in the same order (*21*). In a given

TABLE 2

Elution Volumes in Counts of Low Molecular Weight Solutes in several Eluents (1 count = 0.97 ml).

Eluent[a] (Vol/Vol)	DIMER[a]	ETBZ[a]	MONOM[a]	DICLB[a]	PHENOL[a]
MEK	85.1	87.5	89.6	88.8	90.1
MEK-Methanol (89/11)	84.2	86.7	88.8	88.6	89.2
MEK-Heptane (50/50)	87.7	87.9	89.9	90.6	90.6
THF	89.5	92.2	94.5	94.3	94.7
THF-Methanol (84/16)	85,2	89.0	92.1	91.7	93.2

a) MEK = butanone ; THF = tetrahydrofuran ; DIMER = α, methyl styrene dimer ; ETBZ = ethyl benzene ; MONOM = styrene monomer ; DICLB = o,dichlorbenzene ; PHENOL = phenol .

family of eluents (MEK-based or THF-based mixtures) the elution volumes of a given solute also hold to the expected behaviour of increasing elution volumes with decreasing $\varepsilon°$. The exceptions to that general trend are presented by the elution volumes of o,dichlorbenzene and the monomer, which, are in general in the inverse order to that expected from their δ values. It is true that the o,dichlorbenzene molecular size is larger than that of styrene and if molecular-sieve effects are still present they would work decreasing the retention volumes of the o,dichlorbenzene and explaining in part the found discrepacies. However, we believe that the complete explanation to this anomalous behaviour must be found on the exact nature of solute-substrate interactions. To this respect, a look to the contributions to δ due to dispersion forces (δ_d), to polar forces (δ_p) and to hydrogen bonding (δ_h), according to the scheme proposed by Hansen (*22*), may be worth. In table 3 the three dimensional solubility parameters of table 2 solutes, exception made of the α,methyl styrene dimer, are shown. The solutes are not only arranged in order of increasing δ but also in order of increasing δ_d, δ_p and δ_h. Again, the exception to this general trend arise in the o,dichlorbenzene and styrene δ_h values, the discrepacies being parallel to those found in their elution volumes. This parallelism

TABLE 3

Three Dimensional Solubility Parameters, according to Hansen's scheme (*21*)

Solute	δ	δ_d	δ_p	δ_h
Ethyl benzene[a)]	8.80	8.70	0.3	0.7
Styrene[a)]	9.30	9.07	0.5	2.0
o,dichlorbenzene[a)]	9.98	9.35	3.1	1.6
Phenol[b)]	11.4	9.5		

a) From reference (*23*)
b) From reference (*21*)

seems to indicate that solute-substrate interactions are in this case similar to those known to be displayed by small molecules (ketones, alcohols and acids), which adsorb on the silanol groups via hydrogen bonding (*24*).

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