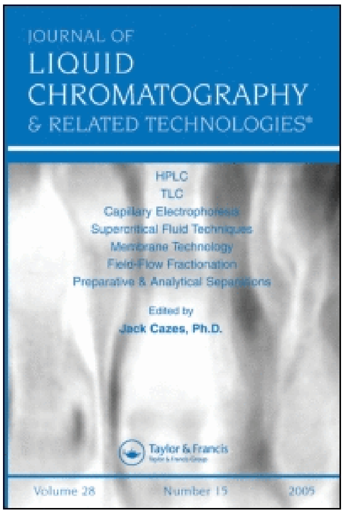

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Influence of Solvent Polarity on Elution Volume in the Case of Polar Polymers

H. J. Mencer[a][b]; Z. Grubisic-gallot[a]
[a] Centre de Recherches sur les Macromolécules (CNRS) 6, Strasbourg-Cedex, France [b] Technol. Dept, Institute of Physical Chemistry, University of Zagreb,

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INFLUENCE OF SOLVENT POLARITY ON ELUTION VOLUME IN THE CASE OF POLAR POLYMERS

H.J. Mencer* and Z. Grubisic-Gallot
Centre de Recherches sur les Macromolécules (CNRS)
6, rue Boussingault
67083 Strasbourg-Cedex, France

ABSTRACT

The influence of solvent polarity on elution volume has been studied in the case of polar polymers such as homopoly-2-vinylpyridine and polystyrene-poly-2-vinylpyridine block or graft copolymers eluted on crosslinked polystyrene gels in tetrahydrofuran or dimethylformamide medium.

INTRODUCTION

The importance of gel permeation chromatography (GPC) as a method of characterizing the molecular weight distribution of polymer materials has been widely recognized. It was shown (1) many years ago that the universal calibration method gives a relationship between the hydrodynamic volume ($[\eta]$ M) and the elution volume (Ve) and is valid for homopolymers and copolymers in eluents that are compatible with the gel (2). In this case, the solutes do not display preferential affinity for either the mobile or stationary phase, which means that the only mechanism of separation is steric exclusion controlled by solute size (3).

The aim of this work was to compare GPC behaviour of some previously uncharacterized systems containing solvents and polymers of different polarities and to find out to what extent a universal calibration can be applied to such systems.

EXPERIMENTAL

The GPC data were obtained with a Waters Associates model 200 gel permeation chromatograph at constant room temperature. The flow rate of 1ml min^{-1} was obtained from a high-pressure Waters pump, model 6000. Distilled tetrahydrofuran (THF) and dimethylformamide (DMF) (4) were used. In the case of THF as solvent, six Styragel columns (120cmx7.6mm I.D.) were used with exclusion limits 10^7, 10^6, $3\text{x}10^5$, $3\text{x}10^4$, $3\text{x}10^3$ and $5\text{x}10^2$ Å. The set of Styragel columns used with the DMF is 10^7, 10^6, 10^5, 10^4 and 10^3 Å.

Anionically prepared polystyrene (PS) standards were obtained from Pressure Chemical Co. and our laboratory. Homopoly-2-vinylpyridine (P2VP) and polystyrene-poly-2-vinylpyridine (PS-P2VP) block or graft copolymers were synthesized in our Institute (5) via anionic polymerization.

The intrinsic viscosities of all the samples investigated were determined in THF and DMF at 298K with an automatic viscometer (6).

RESULTS AND DISCUSSION

In the first part of this work, the behaviour of poly-2-vinylpyridine (P2VP) in tetrahydrofuran (THF)/Styragel system was compared with that of the reference polystyrene (PS)/THF/Styragel system. P2VP and PS have similar structure but the lone electron pair on the nitrogen atom in P2VP makes it more polar than PS. The PS/THF/Styragel system is most often used as a model system. It has been suggested (7) that preferential interactions among components in this system can be neglected, so that it can be used as a reference.

For this study a new series of Styragel columns have been used. Indeed,we have observed that with usage of the columns P2VP is retained on the gel when THF is employed as the elution solvent. It is probably for this reason that some authors (8) have concluded that P2VP could not be characterized in THF by using Styragel columns. In our measurements we have obtained symetric and reproductible chromatograms, the amount of recovered polymer corresponding to the quantity of injected polymer. The results are presented in Table 1 and Figures 1-3.

Figure 1 gives the specific calibration curve (log M vs V_e) for both homopolymers. In this figure experimental results relative to some of the PS-P2VP block or graft copolymers are also plotted. Figure 2 shows the dependence of log$[\eta]$ on the elution volume for both homopolymers. Such a plot is uncommon when GPC results are discussed, but it seemed appropriate to be used in this work. In Figure 3, log$[\eta]$ M vs V_e calibration curves are given.

Figure 1 shows that both curves in the low molecular weight region have the same slopes, for a given molecular weight the elution volume being higher for P2VP than for PS. Different slopes for these two polymers might have been expected (9), due to the fact that THF is a better solvent for PS than for P2VP. This is

TABLE 1

Viscosity and elution volume values in THF

Sample	M_w	$[\eta]$(ml/g)	V_e(counts)
PS	10,300	11.0	47.2
	19,900	15.3	45.7
	51,000	30.0	43.5
	98,200	46.6	42.1
	411,000	127.6	37.8
	670,000	183.4	36.5
P2VP	6,000	5.1	48.7
	9,900	6.0	47.8
	14,000	8.3	46.9
	28,000	14.1	45.3
	68,000	26.0	43.7
	134,000	35.5	43.2
PS-P2VP Copolymer	17,000	11.3	46.2
	26,800	19.6	44.8
	28,000	14.4	45.5
	143,000	39.9	42.8
	240,000	69.7	42.3

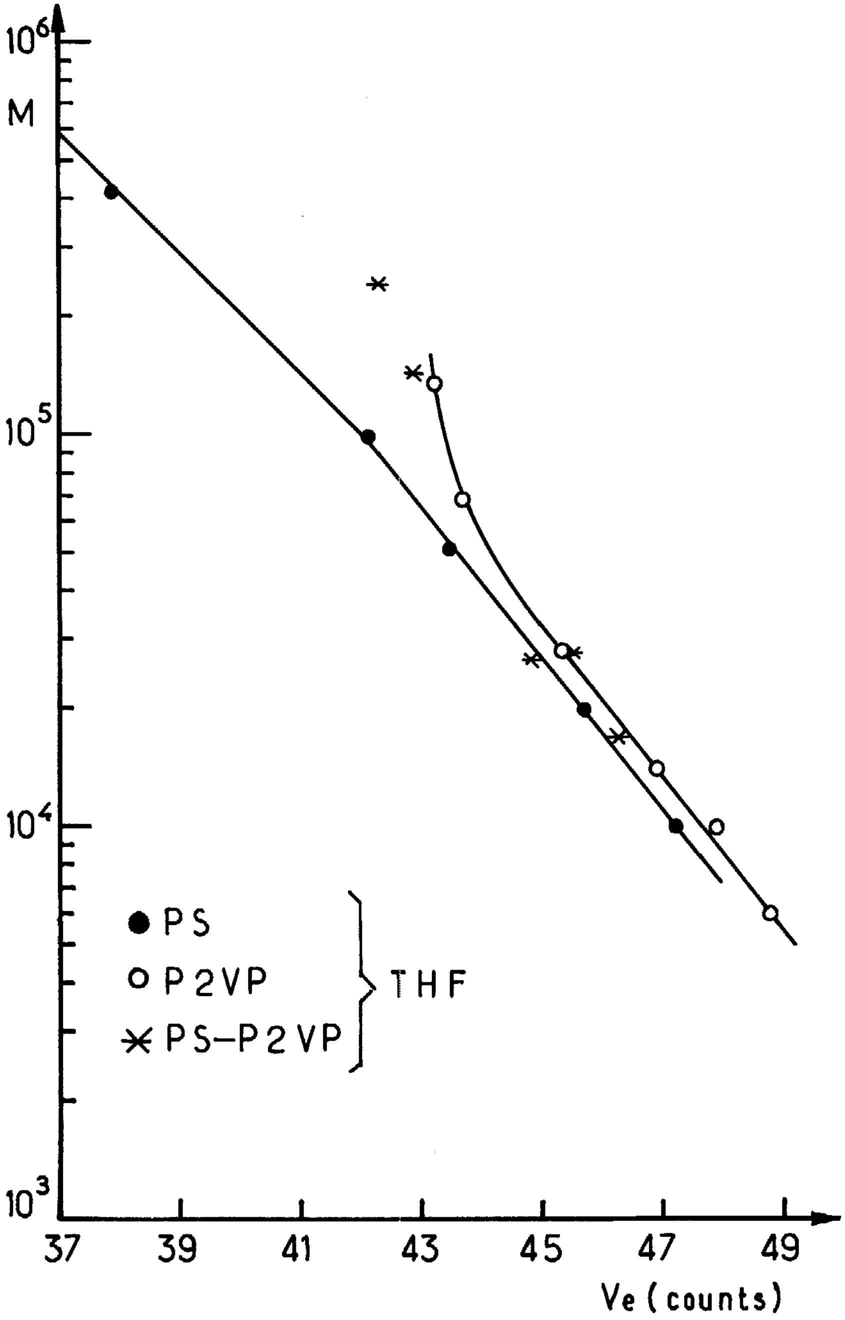
10^6
M
10^5
10^4
10^3
● PS
○ P2VP
✳ PS–P2VP
THF
37
39
41
43
45
47
49
Ve (counts)

FIGURE 1

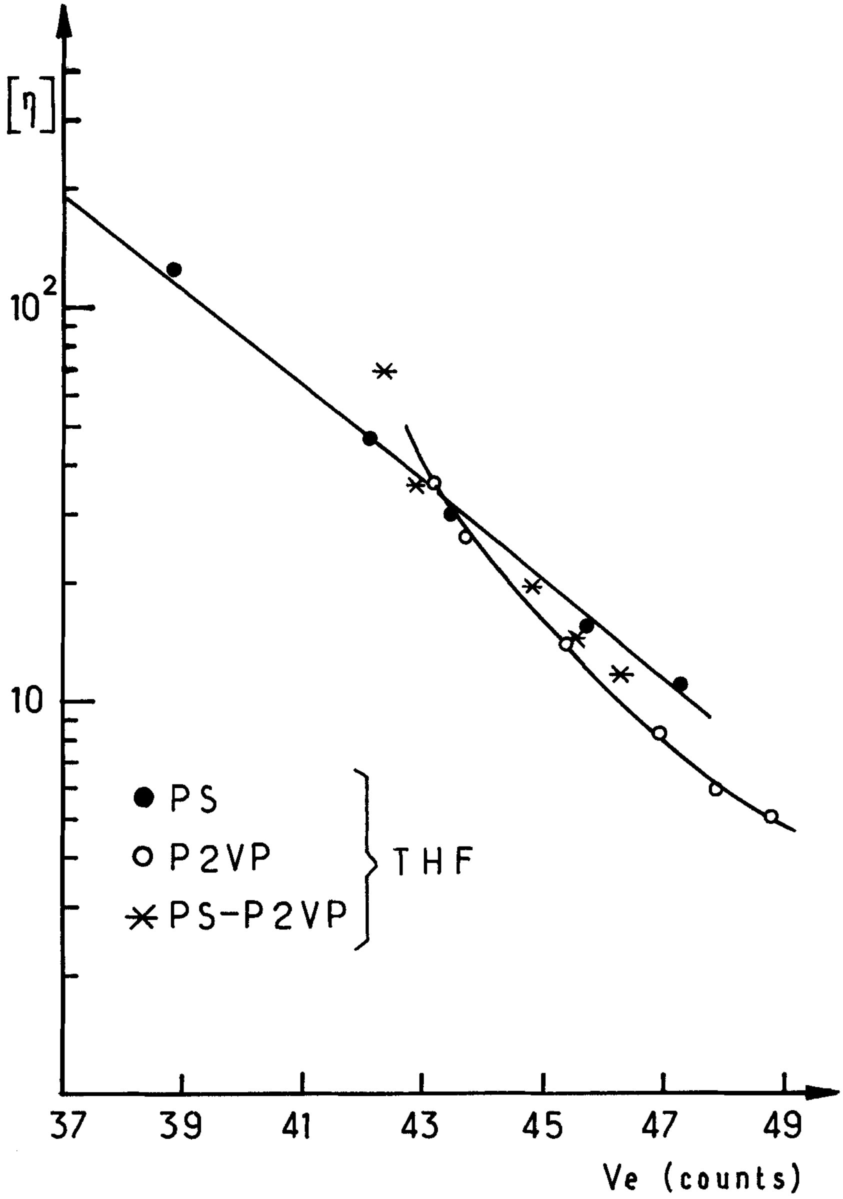

FIGURE 2

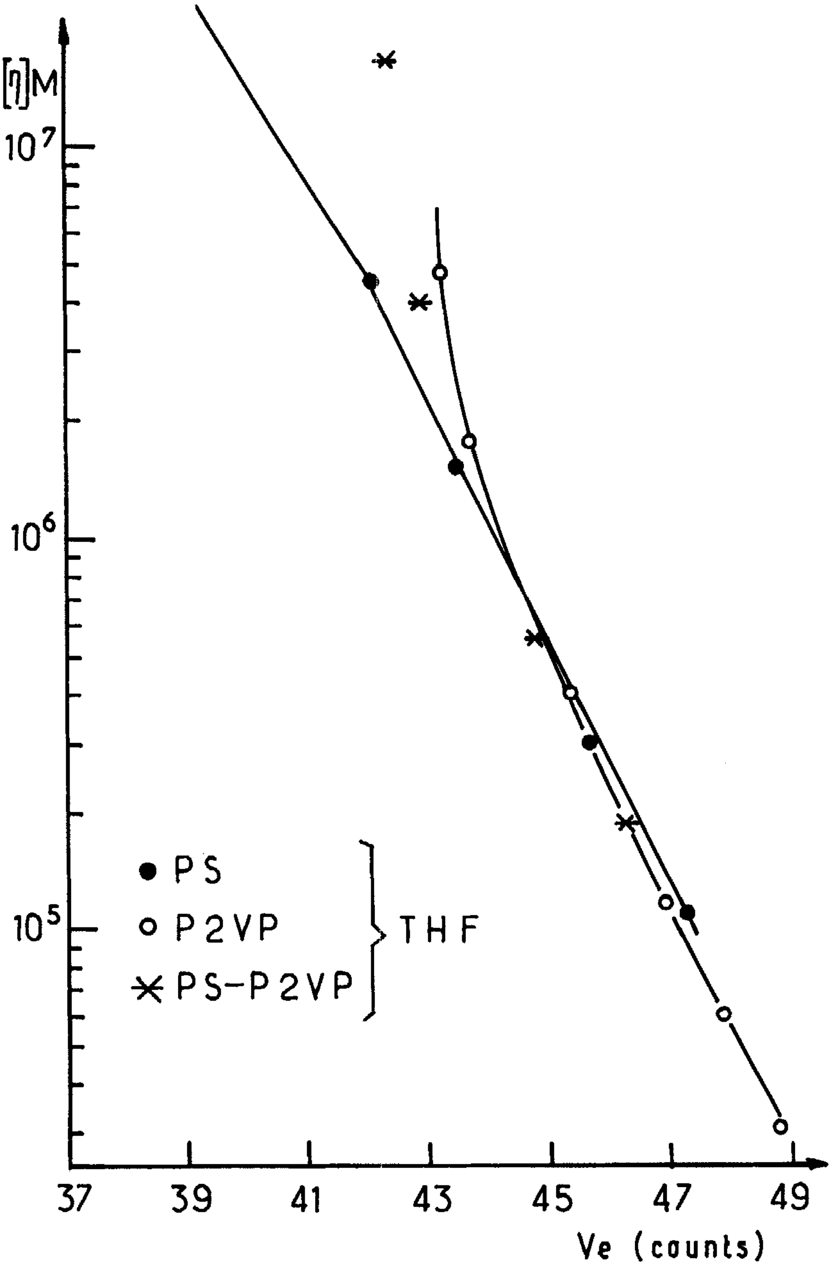

FIGURE 3

shown by the viscometric results which give different values of α for both polymers in THF at 298K.

$[\eta] = 1.18\mathrm{x}10^{-2}\ M_w^{0.709}$ for PS (molecular weight range : $1.0\mathrm{x}10^4 - 9.55\mathrm{x}10^5$)

$[\eta] = 1.49\mathrm{x}10^{-2}\ M_w^{0.663}$ for P2VP (molecular weight range : $6\mathrm{x}10^3 - 1.34\mathrm{x}10^5$)

The difference in α values explains the shift of the P2VP curve to the right and suggests a steeper slope for this curve. Since the latter effect was not observed in the low molecular weight region,it seems reasonable to assume the existence of an additional separation mechanism. To obtain better understanding of the nature of such a secondary mechanism, which is most probably due to preferential interactions among components in GPC system, it is illustrative to take into consideration solubility parameters for all the components (Table 2).

Solubility parameter values for PS, THF and Styragel are practically the same, but its value differs for P2VP. Interactions between gel and eluent in the system P2VP/THF/Styragel are favoured-P2VP is"repulsed" from the gel - which means that P2VP molecules are eluted earlier than expected.

The effect must be larger for smaller P2VP molecules, which are expected to penetrate deeper into the gel pores. At higher molecular weights, the slope of the P2VP curve changes because the secondary separation effect diminishes.

The curves presented in Figure 2 show the influence of solvent-polymer interactions in GPC columns. The positions of both

TABLE 2

Solubility parameter values

Sample	$\delta(\mathrm{J}\ /\mathrm{m}^3)^{1/2}\mathrm{x}10^{-3}$
THF	18.6
PS	18.6
$\mathrm{PS}_{\mathrm{gel}}$	18.6
P2VP	21.5

curves in such a diagram is inverse in relation to that in the specific calibration (Figure 1). The curve corresponding to P2VP is located at lower elution volumes than the curve for PS, although the former polymer exhibits a lower α value, which means lower hydrodynamic volumes. This directly shows the presence of the secondary separation effect.

The universal calibration curves given in Figure 3 represent the combination of curves plotted in Figures 1 and 2. The close fit of both curves appears therefore to be the result of coincidence of specific interactions in P2VP/THF/Styragel system.

Experimental points representing copolymer PS-P2VP systems are located in all three diagrams between the curves typical for homopolymers.

The behaviour of PS and P2VP in GPC columns filled with Styragel was further investigated with DMF, a typical polar aprotic solvent (Table 3). Its component due to polar forces of solubility

TABLE 3

Viscosity and elution volume values in DMF

Sample	M_w	$[\eta]$(ml/g)	V_e(counts)
PS	18,500	10.5	32.0
	40,000	20.0	30.1
	82,000	26.0	28.7
	213,000	49.3	26.1
	320,000	66.3	25.2
	620,000	97.5	23.8
	934,000	115.9	23.3
P2VP	6,000	4.8	31.6
	9,900	7.3	30.8
	14,000	10.3	30.0
	28,000	16.4	28.8
	68,000	29.7	27.4
	134,000	47.7	26.3
PS-P2VP Copolymer	17,000	14.7	30.5
	26,800	16.3	29.5
	28,000	15.2	30.3
	133,000	29.5	26.6
	143,000	29.8	26.7
	240,000	65.0	25.2

parameter $\delta_p = 13.7\text{x}10^3\ (\text{J/m}^3)^{1/2}$ is significantly different from the corresponding value of THF, $\delta_p = 5.7\text{x}10^3\ (\text{J/m}^3)^{1/2}$. The GPC results obtained with system PS/DMF/Styragel and P2VP/DMF/Styragel are shown in Figures 4-6. Again, the specific log M vs V_e calibration is given in Figure 4, $\log[\eta]$ vs V_e in Figure 5 and $\log[\eta]M$ vs V_e calibration in Figure 6.

Typical curves for P2VP in Figure 4 and 5 are located at lower elution volumes in relation to curves for PS, which means that P2VP molecules are eluted from the columns earlier than the corresponding PS molecules. The same trend is therefore obvious in the "universal" calibration curve.

Viscometric results obtained with PS in DMF and P2VP in DMF at 298 K lead to the following relations :

$[\eta] = 4.65\text{x}10^{-2}\ M_w^{0.609}$ for PS (molecular weight range : $1.85\text{x}10^4 - 9.34\text{x}10^5$)

$[\eta] = 9.1\ \text{x}10^{-3}\ M_w^{0.728}$ for P2VP (molecular weight range : $6\text{x}10^{-3} - 1.34\text{x}10^5$)

The α values show that DMF is a better solvent for P2VP than for PS. The calibration curve for PS in Figure 4 should therefore be steeper than that for P2VP, which is not the case. On the other hand, the lower α value for PS shows that for a given molecular weight the PS molecules have smaller dimensions than P2VP molecules, which reflects in the higher elution volumes of the former polymer. However, such an effect cannot be responsible for very wide difference in elution volumes of relatively similar molecules. These results suggest again the presence of a secondary separation mechanism which affects the slopes of calibration curves and their spacing.

Similarly,the wide spacing observed between PS and P2VP curves in Figure 5 cannot be explained only on the base of a steric exclusion mechanism.

The secondary separation mechanism appears to be active in both investigated systems. In the system PS/DMF/Styragel, there are significant interactions between PS and Styragel (10) resul-

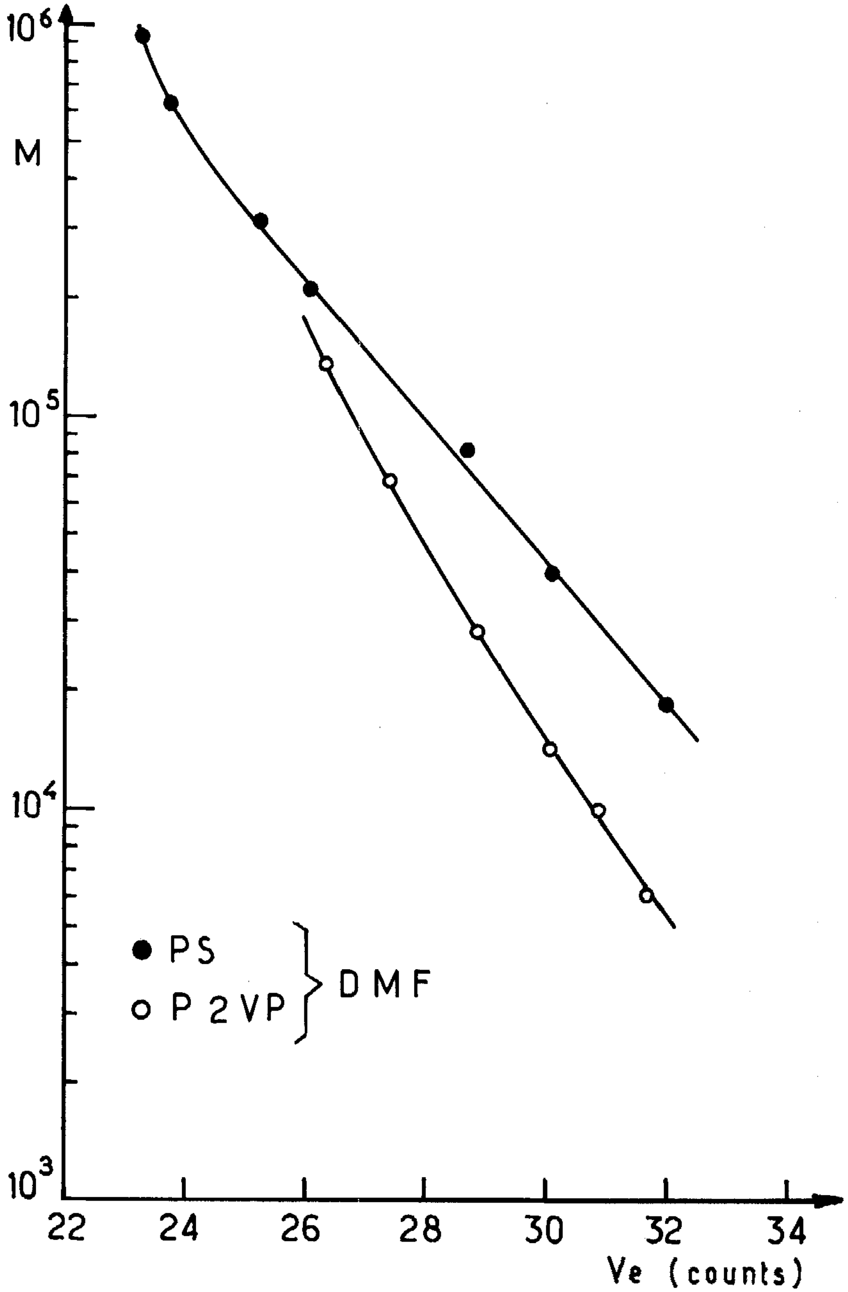

FIGURE 4

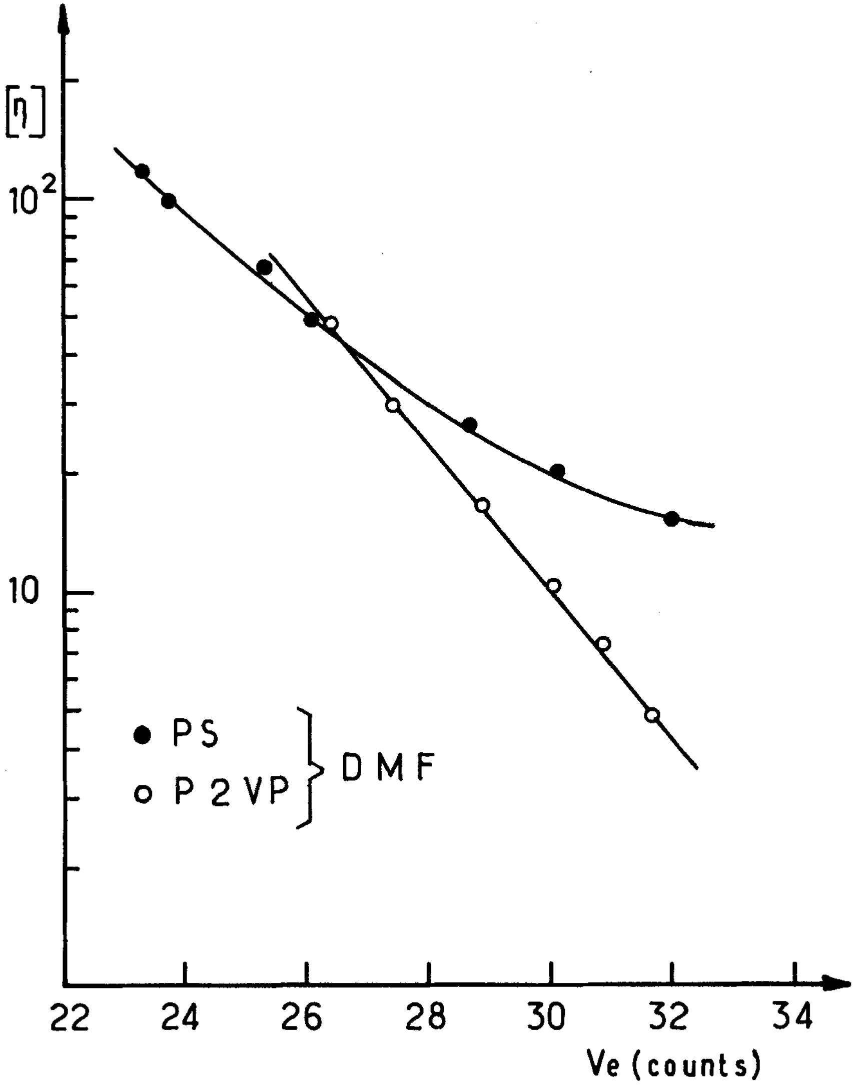

FIGURE 5

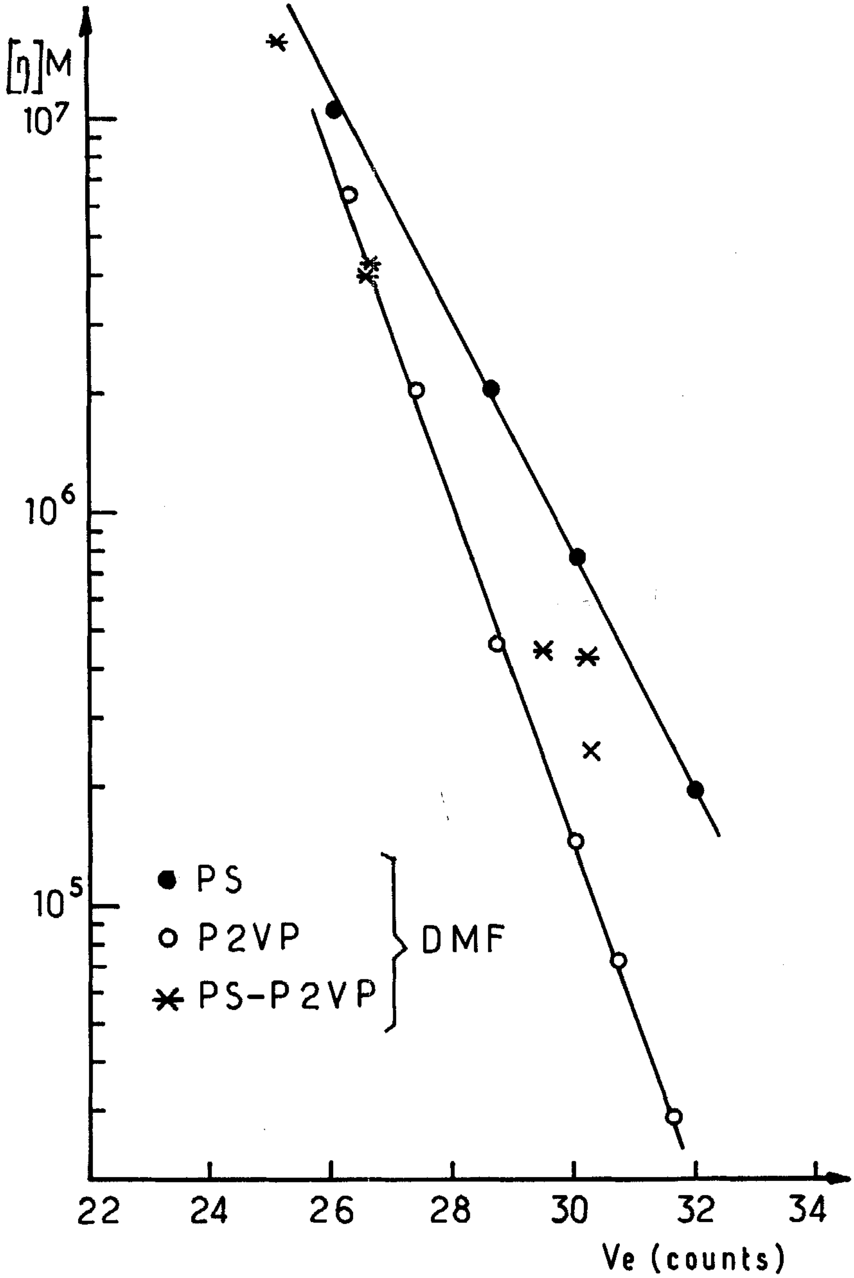

FIGURE 6

ting in the slower elution of the polymer. In the second system, P2VP/DMF/Styragel, strong interactions between DMF and polar P2VP can be assumed, so P2VP is "repulsed" from the gel. P2VP molecules are therefore eluted earlier than expected from the steric exclusion mechanism only, and such an effect is manifest in the steeper slope of calibration curve in Figure 4.

The consequence of such behaviour is seen in Figure 6 giving two $\log[\eta]M$ vs V_e calibration curves, which are very widely spaced.

The experimental points for copolymers in DMF are located again between two curves for the homopolymers, the elution volume for a given $[\eta]M$ value being a function of the chemical composition of the copolymer.

CONCLUSION

Conditions of GPC separation of PS and P2VP as well as their copolymers on Styragel in two different solvents (THF and DMF) have been compared. It was shown that in all systems investigated, except PS/THF/Styragel, the separation mechanism is complex, consisting of at least two effects. Therefore, it is difficult to use the universal calibration in the case of systems for which steric exclusion is not the only separation mechanism.

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* Present address : Institute of Physical Chemistry, Technol. Dept
University of Zagreb

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