Gel Permeation Chromatography of Poly(*N*-vinyl-3,6-dibromocarbazole). Universal Calibration, Nonexclusion Effects, and Incompatibility

J. M. Barrales-Rienda and P. A. Galera Gômez

Instituto de Plásticos y Caucho, CSIC, Madrid 28006, Spain

A. Horta*

Departamento de Quimica General y Macromoléculas, Facultad de Ciencias, Universidad a Distancia, Madrid, 28040, Spain

E. Sáiz

Departamento de Quimica-Fisica, Facultad de Ciencias, Universidad de Alcalá de Henares, Alcalá de Henares, Madrid, Spain. *Received March 6, 1985*

ABSTRACT: Nonexclusion effects in the GPC of poly(*N*-vinyl-3,6-dibromocarbazole) (PVK-3,6-Br_2) in tetrahydrofuran, at 25 °C, using cross-linked polystyrene (PS) as the gel phase, are analyzed by use of the universal calibration method. The first point in order to determine such nonexclusion effects is to use values for the hydrodynamic volume and the elution volume truly representative of the samples. We show that an adequate set of average magnitudes is the weight-average intrinsic viscosity of the sample, the viscosity-average molecular weight, and the elution volume defined as the viscosity average by means of $\bar{V}_{v,i} = \log \{\int_0^\infty H_i(V)[10^{aA_1V}]\, dV\}^{(1/aA_1)}$, where $H_i(V)$ represents the relative weight of the normalized chromatogram for sample i at elution volume V, a is the exponent in the Mark–Houwink equation for the system under study, and A_1 is the coefficient of the linear term in the log M vs. V calibration of GPC valid for samples constituted of monomolecular species. The early elution of PVK-3,6-Br_2 in THF, as compared with PS standards, can be represented by the equation $V_e = V_0 + K_D K_p V_i$, where V_e is the retention volume, V_0 the interstitial volume, V_i the solvent volume within the gel, K_D the distribution coefficient for steric exclusion, which is given by $K_D = -A \log ([\eta]M) + B$ (A and B are constants), and K_p is a distribution coefficient for solute–gel interactions. The values of K_p found in the present system are below unity, and their molecular weight dependence can be represented by $-\ln K_p \sim X_2$, where X_2 is the degree of polymerization of the polymer molecule in the mobile phase. In the formulation of Dawkins this corresponds to incompatibility between eluted polymer (2) and gel (3), and $-\ln K_p/X_2 = \phi_3(1 + \chi_{23})$, where ϕ_3 is the volume fraction of the gel in the stationary phase and χ_{23} the polymer–gel interaction parameter per polymer repeating unit. The compatibility of PVK-3,6-Br_2 with PS in THF solution is studied by determining the phase-separation diagram of the ternary system THF (1) + PVK-3,6-Br_2 (2) + linear PS (3), from which a value of χ_{23} at the plait point is determined. The equilibrium distribution of solute polymer (2) between the mobile phase and the gel is treated thermodynamically as a problem in preferential sorption in a ternary system (selective adsorption or desorption of 2 by 3 from the 1 + 2 solution). The result of this thermodynamic treatment is $-\ln K_p/X_2 = \phi_3(1 + g_{23} - g_{12} - g_{13})$, which is similar to the one given by Dawkins, but now it includes the additional contribution of the polymer–solvent and gel–solvent interaction parameters g_{12} and g_{13}. These g_{ij}'s and the χ_{ij}'s defined on the basis of chemical potential are connected through $\chi_{ij} = g_{ij} - (1 - \phi_j)(\partial g_{ij}/\partial \phi_j)$. The value of $g_{12} + g_{13}$ can be of the order of unity so that $(1 - g_{12} - g_{13})$ can approximately cancel. This expression gives thus the conditions under which K_p can be unity or differ from unity depending on the balance of the interaction parameters.

Introduction

As has been recognized for a long time, steric exclusion from a theoretical point of view is the only separation mechanism in gel permeation chromatography (GPC). However in practice there exist some other effects such as solvation of the macromolecular species, adsorption on the wall of the pores, dissolution inside the gel, incompatibility between the solute and the gel, and secondary exclusion that greatly disturb solute exclusion and therefore invalidate to a great extent the universal calibration concept for polymers.[1–5]

Grübisic-Gallot et al.[6,7] were the first to suggest that the hydrodynamic volume ($V_h = [\eta]M$) should be used for universal calibration in GPC, showing that a plot of log V_h vs. elution volume (V_e) was the same within experimental error for homopolymers and copolymers having various chemical structures. The relation was also unaffected when solvents of unlike polarity were used, at least in the solvent–polymer systems investigated.

This universal calibration method, however, cannot be valid when variable interactions occur between the polymer and the stationary phase, since elution volume is then governed, in part, by factors that are not reflected in their hydrodynamic dilute-solution properties.[1]

The interpretation of results from GPC on poly(*N*-vinyl-3,6-dibromocarbazole) (PVK-3,6-Br_2) is much more complicated than in the case of many other linear vinyl polymers. This may be because this macromolecule is composed of structural units having not only bulky side groups leading to a certain type of stiffness but also side groups containing strongly polar groups. Whilst the presence of bulky side groups in the vinyl polymer[6,8,9] does not seem to have any remarkable effect on the GPC, polar groups should affect the determination appreciably. In addition, gel permeation chromatograms could not be used in a conventional manner to derive reliable values of $\bar{M}_w/\bar{M}_n$ through the universal calibration for polymers because of peak extrabroadening due to the solute–gel interaction known for some nitrogen-containing polymers.[10,11]

The constants in the Mark–Houwink equation, i.e., $[\eta] = KM^a$ have been determined for this polymer by classical methods in good[12] and Θ solvents,[13] permitting calculation of the polymer unperturbed dimensions and by more elaborate methods using gel permeation chromatography.[14]

In gel permeation chromatography, when one intends to analyze nonexclusion effects, the most important step in the data interpretation is to establish the true location

0024-9297/85/2218-2572$01.50/0

Table I
Averages of Molecular Weight, Intrinsic Viscosity, Gel Permeation Chromatography Data, and K_p[a]

fraction	$\bar{M}_n$[b] $\times 10^{-3}$	$\bar{M}_w$[c] $\times 10^{-3}$	$\bar{M}_w/\bar{M}_n$[d]	$\bar{M}_v \times 10^{-3}$	[η], mL/g	$\bar{V}_v$, counts	V_e(peak), counts	K_p
F-3		602	1.21	634	57.2	29.30	31.6	0.54
F-4		492	1.23	500	47.0	30.08	32.0	0.62
F-5	284	333	1.46	314	32.0	31.62	32.8	0.74
F-6		303	1.39	272	28.4	32.09	32.9	0.77
F-7	203	285	1.43	274	28.6	32.07	33.0	0.77
F-8	175	208	1.34	206	22.6	33.01	33.8	0.82
F-9	142	166	1.23	150	17.4	34.05	34.9	0.88
F-10	96.6	129	1.14	114	13.8	34.98	35.8	0.92
F-11	63.0	78.0	1.14	84	10.7	36.00	36.7	0.96
F-12	39.5	48.0	1.13	48	6.8	37.81	37.8	1.02

[a] Distribution coefficient for solute–gel interactions for poly(*N*-vinyl-3,6-dibromocarbazole) (PVK-3,6-Br$_2$) fractions in tetrahydrofuran at 25 °C utilizing columns packed with polystyrene gel. [b] Membrane osmometry. [c] Light scattering. [d] Calculated from GPC chromatograms.

of the hydrodynamic volume vs. elution volume calibration plot. True plots may be precisely located when we have at our disposal well-characterized fractions of the polymer to be analyzed if the polydispersity index $\bar{M}_w/\bar{M}_n$ is less than 1.1. In this case, any of the existing criteria may be used to obtain a good description of nonexclusion effects. However, this is not always the case and if the available fractions are appreciably polydisperse none of the existing criteria on hydrodynamic volume and volume of elution can be used without imprecisions in the interpretation of the experimental data.

In order to test the validity of the universal calibration plot for our polymer PVK-3,6-Br$_2$, it is necessary to establish unambiguously a precise relationship between hydrodynamic volume V_h and its respective elution volume V_e.

In the present paper we use experimental data determined on broad molecular weight distribution samples. It is thus of utmost importance to obtain adequate averages for [η], M, and V_e in order to check the validity of the universal calibration in our system.

To calculate such averages we develop here a numerical method, similar to the one applied before for the self-calibration of molecular weight in GPC columns when narrow MWD standards are not available.[15] With such a method we treat the intrinsic viscosity and $\bar{M}_v$ data and the chromatograms of the fractions to obtain the proper averages of [η], M, and V_e, which ought to be used in order to establish the correct relationship between hydrodynamic volume and elution volume. This method may be useful and free from error sources when universal calibration is impractical due to the existence of some secondary exclusion effects (adsorption, solvation, incompatibility, etc.) or to the suspected inadequacy of the existing Mark–Houwink parameters when the method of Coll and Gilding[16] is intended to be used. As is well-known, the use of this method to give reliable results is severely restricted to samples for which parameters in its respective Mark–Houwink equation are supposed to be known for the same conditions as those employed for GPC measurements, i.e., solvent, temperature, polydispersity of the fractions, etc.

Another objective of the present work, which has been undertaken in connection with the interpretation of our GPC experimental data, was to explore the compatibility or incompatibility of the polystyrene and poly(*N*-vinyl-3,6-dibromocarbazole) system with tetrahydrofuran as the solvent and to assign polymer–polymer interaction parameters. To this end we have performed phase separation experiments in the ternary system THF (1) + PVK-3,6-Br$_2$ (2) + PS (linear) (3).

Experimental Section

Materials. The most characteristic molecular constants and GPC data of the ten fractions of PVK-3,6-Br$_2$ employed in the present work have been given elsewhere.[14] The values of some of these characteristics and molecular constants are given in Table I.

Polystyrene (PS). A polydisperse polystyrene sample obtained from Dow Unquinesa, S.A., was used in the study of the cloud-point curve (CPC) for the ternary system. Its weight-average molecular weight measured with a Sofica light scattering instrument at 5461 Å using toluene as the solvent at 25 °C was $\bar{M}_w = 3.34 \times 10^5$, and its intrinsic viscosity estimated in the same solvent and temperature was [η] = 98.8 mL/g. It corresponds to a viscosity-average molecular weight[17] of $\bar{M}_v = 2.73 \times 10^5$.

Poly(*N*-vinyl-3,6-dibromocarbazole) (PVK-3,6-Br$_2$). As the PVK-3,6-Br$_2$ sample for the CPC study, we have used a polydisperse sample whose synthesis and characterization has been described elsewhere.[18] Its weight-average molecular weight determined with a Sofica light scattering instrument at 5461 Å using THF as the solvent at 25 °C was $\bar{M}_w = 4.36 \times 10^5$. Its intrinsic viscosity estimated in THF at 25 °C was [η] = 35.6 mL/g. Its weight- and number-average molecular weights estimated from fractionation data are $\bar{M}_w = 4.22 \times 10^5$ and $\bar{M}_n = 1.88 \times 10^5$ ($\bar{M}_w/\bar{M}_n = 2.24$), respectively.[18]

Density. Density of the unfractionated sample of PVK-3,6-Br$_2$ has been measured by means of a flotation technique using potassium iodide (Merck, A.G.) aqueous solutions; $d^{20}{}_4 = 1.7724$ g/mL. The density for PS at 25 °C has been obtained by interpolation from the data given by Matheson et al.[19] $d^{25}{}_4 = 1.053$ g/mL. The tetrahydrofuran employed through the study as the solvent in the ternary system was the same used for GPC experiments.[14] The density of THF was taken as 0.883 g/mL at 25 °C.[20]

Phase Separation Experiments. Measured amounts of polystyrene (PS) and PVK-3,6-Br$_2$ were dissolved in a given volume of THF. The solution was then kept at 25 °C for 24 h to establish the solution for both polymers in the solvent. From this solution, the solvent was evaporated at 25 °C under agitation through an oil pump and liquid-nitrogen trap until the solution showed turbidity. At this point the solution was allowed to stand for a period of 2–3 h. Then dropwise addition of the solvent was carried out slowly to permit the clarification point to be detected. The appearance and disappearance of the cloudiness upon slight rewarming (30 °C) and recooling (20 °C) to the former temperature (25 °C), respectively, were also checked. Thus, the boundary point was determined, and the weight of the three components at this point were indicated by the weight fractions, i.e., w_1, w_2, and w_3 for THF, PVK-3,6-Br$_2$ and PS, respectively. The results of this system are presented as the phase diagram given in Figure 1.

Polystyrene Standards. The PS standards used to obtain the PS calibration were obtained from Water Associates, Pressure Chemical Co., and Centre de Recherches sur les Macromolecules. The polymer concentrations were 0.2% (20 mg/10 mL).

Gel Permeation Chromatography. Gel permeation chromatography experiments were performed at 25 °C with THF as eluent by using a Waters Associates Model 200 gel permeation chromatograph. THF employed as the solvent was distilled from copper(I) chloride and potassium hydroxide. A series arrangement of five polystyrene gel columns, with nominal exclusion sizes of 10^7, 10^6, 10^5, 10^4 and 3×10^3 Å (Waters designation), was used. Elutions were conducted with a flow rate of 1 mL/min. Elution volumes (counts) were calculated from the initial point of injection

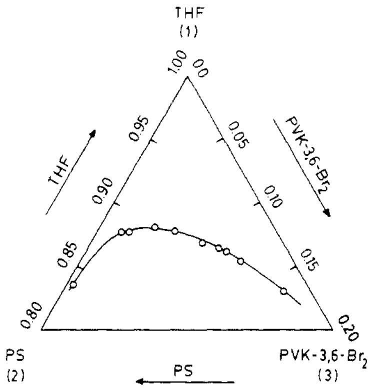

Figure 1. Phase separation diagram in the system tetrahydrofuran (THF) + poly(*N*-vinyl-3,6-dibromocarbazole) (PVK-3,6-Br$_2$) + polystyrene (PS) at 20 °C.

to the appearance of the peak height maximum of the gel permeation chromatograms. Polymer concentrations (w/v) were 0.2–0.3 nw/v), all the polymer in the sample loop being injected. Injections of 120 s for the sample solutions were used.

Results and Discussion

Hydrodynamic Volume. The concept of universal calibration[6,7] establishes that the hydrodynamic volume of a polymer molecule is the property that determines its elution volume in GPC. The hydrodynamic volume of a single macromolecule is proportional to the product of its molecular mass and its intrinsic viscosity: $[\eta]M$. Therefore, the universal calibration law can be written as

$$\log ([\eta]M) = f(V) \tag{1}$$

where $f(V)$ means a uniform function of V. Equation 1 holds strictly for a single molecular or monodisperse species. The problem when dealing with polydisperse samples, as is the most frequently encountered case, is to know the appropriate averages that should be used for $[\eta]$, M, and V in order to maintain the validity of 1.

In a previous paper[15] some of the present authors have employed a series of procedures to obtain the parameters of the GPC calibration equation

$$\log M = A_0 + A_1 V + A_2 V^2 + \ldots + A_n V^n \tag{2}$$

The methods were also extended by us to get the true Mark–Houwink equation parameters K and a by means of[14]

$$\log [\eta] = \log K + a \log M \tag{3}$$

The methods when applied to eq 2 as well as to eq 3 give results for the coefficients of such equations that are valid for samples constituted of monomolecular species independently if they have been obtained from average properties measured on polydisperse samples. Combining eq 2 and 3 to obtain the hydrodynamic volume, we get for a monomolecular species

$$\log ([\eta]M) = \log (KM^{1+a}) = \log K + (1 + a)(A_0 + A_1 V + \ldots) = \log K + (1 + a)A_0 + (1 + a)A_1 V + \ldots \tag{4}$$

namely

$$\log ([\eta]M) = C_0 + C_1 V + \ldots \tag{5}$$

with

$$C_0 = \log K + (1 + a)A_0$$
$$C_1 = (1 + a)A_1 \tag{6}$$
$$\ldots\ldots$$

When dealing with polydisperse samples, the experimental intrinsic viscosity of each sample is a weight average of the intrinsic viscosities of the monomolecular species present in it.[21] However, the same Mark–Houwink equation valid for the monomolecular species holds with the $[\bar{\eta}]$(exptl) of the polydisperse samples if their viscosity-average molecular weights, $\bar{M}_v$, are used in eq 3 in place of M, namely

$$\log [\bar{\eta}] = \log K + a \log \bar{M}_v \tag{7}$$

(K and a having the same values as in eq 3). The product $[\bar{\eta}]\bar{M}_v$ for polydisperse samples is then

$$\log ([\bar{\eta}]\bar{M}_v) = \log K + (1 + a) \log \bar{M}_v \tag{8}$$

If in eq 2 we use an average molecular weight, $\bar{M}$, in place of M, we obtain a corresponding average elution volume, $\bar{V}$ (using the same coefficients A_0, A_1, ..., determined for monomolecular species). With $\bar{M}_v$ in eq 2 we obtain a viscosity-average elution volume, $\bar{V}_v$

$$\log \bar{M}_v = A_0 + A_1 \bar{V}_v + \ldots \tag{9}$$

with $\bar{M}_w$, a weight-average $\bar{V}_w$ and with $\bar{M}_n$, a number-average $\bar{V}_n$.

Substituting $\log \bar{M}_v$ in this way in eq 8, we get

$$\log ([\bar{\eta}]\bar{M}_v) = \log K + (1 + a)A_0 + (1 + a)A_1 \bar{V}_v + \ldots = C_0 + C_1 \bar{V}_v + \ldots \tag{10}$$

Therefore, for polydisperse samples, eq 5 is also valid (with the same coefficients C_0, C_1, ..., corresponding to monomolecular species), provided the product $[\eta]\bar{M}_v$ is used as the hydrodynamic volume and $\bar{V}_v$ is used as the elution volume. $[\eta]$ is determined experimentally directly from the samples, $\bar{M}_v$ is obtained from $[\eta]$ and the Mark–Houwink equation (7), and $\bar{V}_v$ is obtained from $\bar{M}_v$ and the GPC calibration equation (9).

Instead of $\bar{V}_v$ being read off the calibration curve, experimental values of $\bar{V}_v$ can be calculated from the chromatograms. The procedure is as follows. For each sample, i, we calculate its $\bar{M}_{v,i}$ explicitly in terms of the monomolecular M's and their relative weights given by the normalized chromatogram of i, H_i

$$\bar{M}_{v,i} = \left\{\int_0^\infty H_i(V) M(V)^a \, dV\right\}^{1/a} \tag{11}$$

Now, we substitute $M(V)$ according to eq 2

$$\bar{M}_{v,i} = 10^{A_0}\left\{\int_0^\infty H_i(V)[10^{aA_1 V + \ldots}] \, dV\right\}^{1/a} \tag{12}$$

$$\log \bar{M}_{v,i} = A_0 + (1/a) \log \left\{\int_0^\infty H_i(V)[10^{aA_1 V + \ldots}] \, dV\right\} \tag{13}$$

Comparing eq 13 with eq 9 and assuming that the calibration is linear (which in our present experimental case is correct, as shown previously), we get

$$\bar{V}_{v,i} = \log \left\{\int_0^\infty H_i(V)[10^{aA_1 V}] \, dV\right\}^{1/aA_1} \tag{14}$$

Equation 14 can be taken as the definition of the viscosity-average elution volume, $\bar{V}_v$.

Whether the $\bar{V}_{v,i}$'s are calculated from the chromatogram via eq 14 or read off directly from the calibration [eq 9, linear case], equivalent results should be obtained. To check this point we show on Figure 2 $\bar{V}_v$ calculated according to eq 14 (ordinate) plotted vs. $\bar{V}_v$ read off eq 9 (abscissa). We can see that the points distribute more or less at random on either side of the $\bar{V}_v$ (ordinate) = $\bar{V}_v$ (abscissa) diagonal. The agreement, as it is shown, seems to be quite satisfactory, in spite of the errors inherent in the different expermental techniques [gel permeation chromatography, viscometry, membrane osmometry, light scattering, volumetry (siphon), etc.] and those emerging from data fitting and calculations so that both ways of

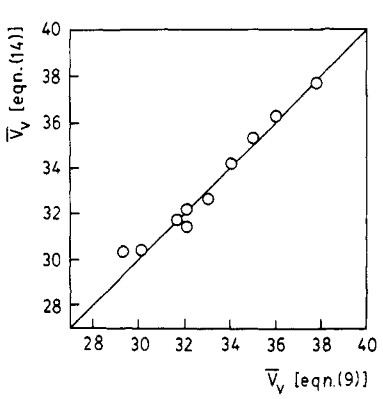

Figure 2. Plot of $\bar{V}_v$ (eq 14) vs. $\bar{V}_v$ (eq 9) for PVK-3,6-Br_2 in tetrahydrofuran at 25 °C utilizing columns packed with polystyrene gel.

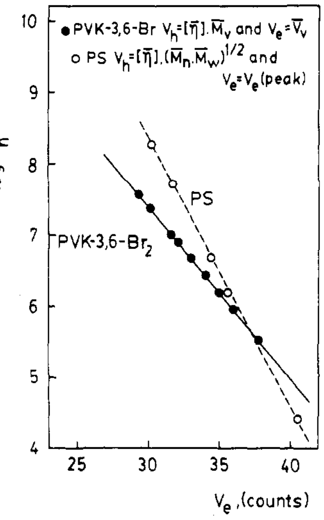

Figure 3. Hydrodynamic volume $V_h = [\bar{\eta}]\bar{M}_v$ vs. retention volume $V_e = \bar{V}_v$ calibration plot for PVK-3,6-Br_2 (●) and hydrodynamic volume $V_h = [\eta]$. $(\bar{M}_n\bar{M}_w)^{1/2}$ vs. retention volume $V_e = V_e$ (peak) calibration plot for PS (○) in tetrahydrofuran at 25 °C utilizing columns packed with polystyrene gel.

calculating the viscosity-average elution volume are in fact equivalent.

The application of the concepts of $[\eta]$, $\bar{M}_v$, and $\bar{V}_v$ of which we have just made mention should be of great utility in an effort to interpret the polystyrene and poly(*N*-vinyl-3,6-dibromocarbazole) elution volume data obtained for THF at 25 °C. Numerical values of all these magnitudes, together with miscellaneous results, are given in Table I.

First of all, we start by determining whether the universal calibration concept holds true with our polymer in comparison with polystyrene. Semilogarithmic plots of hydrodynamic volume vs. elution volume are shown in Figure 3. The full line describes the results for our polymer, PVK-3,6-Br_2. This line has been drawn with log V_h = log $([\eta]\bar{M}_v)$ vs. $\bar{V}_v$, where $[\eta]\bar{M}_v$ corresponds to the values given by eq 10 with $C_0 = 14.590$ and $C_1 = -0.2400$, which have been determined from the values[14] of A_0, A_1, K, and a through eq 6.

The results for the polystyrene standards have been plotted as log $[\eta](\bar{M}_n\bar{M}_w)^{1/2}$ = log V_h vs. V_e (peak) in which $[\eta]$ has been calculated from the Mark–Houwink equation for PS standards in THF at 25 °C given by Spatorico and Coulter[22]

$$[\eta]\ (\text{mL/g}) = 1.10 \times 10^{-4} M_w^{-0.725} \qquad (15)$$

and $(\bar{M}_n\bar{M}_w)^{1/2}$ has been obtained from the data furnished by the suppliers.[14] V_e (peak) represents elution volumes at the peak for the same standards. They are represented by open circles on Figure 3. They yield to a good correlation, which is represented by the dashed straight line.

The plots for the polystyrene standards and poly(*N*-vinyl-3,6-dibromocarbazole) are not coincident and are not parallel. PVK-3,6-Br_2 exhibits unusually low retention volumes relative to its true hydrodynamic volume represented by $V_h = [\eta]\bar{M}_v$; i.e., for a given hydrodynamic volume the elution volume is lower for PVK-3,6-Br_2 than for PS. In addition, the plots shown in Figure 3 clearly demonstrate that eq 1 is not valid to represent the universal calibration as proposed by Benoit et al.[6,7] This plot may be indicating that the interactions between the gel and our PVK-3,6-Br_2 are not always the same. This type of discrepancy and some others that were observed with the universal calibration have very recently been reviewed.[2-4,23,24] It is very important to investigate the elution behavior of our PVK-3,6-Br_2 samples as a function of hydrodynamic volume in a polystyrene network as the gel phase and with tetrahydrofuran as the eluent.

Incompatibility. The aim of this part of the work is to analyze our data, to present evidence for a secondary mechanism process, and to show how our experimental results on PVK-3,6-Br_2 may be interpreted from current theories. The early elution of some polymers in GPC have been interpreted by polymer incompatibility with the gel.[25-29]

Dawkins and Hemming[30] have defined the retention volume V_e by

$$V_e = V_0 + K_D K_p V_i \qquad (16)$$

where V_0 is the interstitial or void volume, V_i is the total volume of solvent within the gel, K_D is the distribution coefficient for steric exclusion, and K_p is the distribution coefficient for solute–gel interactions. Dawkins and Hemming,[30] following a procedure given by Anderson and Stoddart,[31] have proposed the relation

$$K_D = -A \log ([\eta]M) + B \qquad (17)$$

in which it was assumed that hydrodynamic volume is the size parameter determining the steric exclusion separation. A and B are two constants. When eq 17 is substituted into eq 16 the following is given:[2,30]

$$(V_e - V_0)/K_p = V_i(-A \log ([\eta]M) + B) \qquad (18)$$

The representation of this equation for polystyrene and the polymer under study as log $[\eta]M$ vs. $(V_e - V_0)/K_p$ will render information on the separating mechanism taking place between our polymer PVK-3,6-Br_2 and cross-linked polystyrene gel. Thus, for polymers separating solely by steric exclusion K_p is unity. Adsorption and partition mechanisms will both yield $K_p > 1$.

A plot similar to that shown in Figure 3 is obtained when the results are plotted as indicated by eq 18, i.e., log $[\eta]M$ vs. $(V_e - V_0)/K_p$ and taking K_p as unity for both polymers. We have taken $[\eta]M = [\bar{\eta}]\bar{M}_v$ and $V_e = \bar{V}_v$ for our PVK-3,6-Br_2. This clearly indicates that eq 16 does not explain the differences in the behavior between PVK-3,6-Br_2 and PS when the distribution coefficient for the solute-gel interaction (K_p) is taken as unity for both polymers. This also indicates that K_p depends on a certain form of molecular weight.

However, with $K_p = 1$ for PS, a universal calibration plot is obtained if the values of K_p in Table I for PVK-3,6-Br_2 are used.

The values of K_p given in Table I clearly indicate that K_p appreciably depends on molecular weight. In fact, it agrees with the hypothesis advanced by Dawkins[2] that K_p decreases as molecular weight increases, the behavior ex-

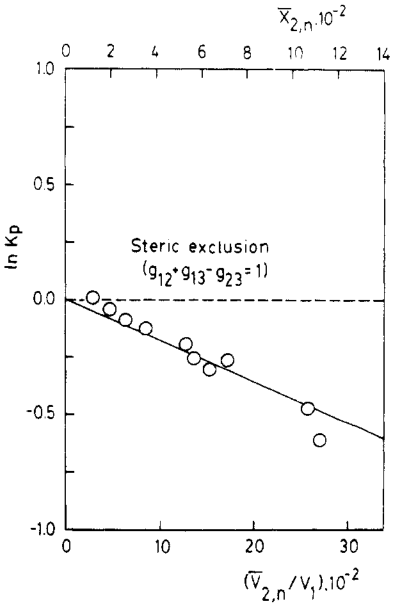

Figure 4. Dependence of ln K_p on the number-average degree of polymerization $\bar{X}_{2,n}$ from data in Table I (top) and dependence of ln K_p on $(\bar{V}_{2,n}/V_1)$ from data given in Table I and Experimental Section (bottom). $\bar{V}_{2,n}$ has been calculated from experimental data by means of $\bar{V}_{2,n} = \bar{X}_{2,n}V_2$; V_2 represents the molar volume of the repeating unit.

pected for K_p if $K_p < 1$ is due to incompatibility between the polymer being eluted and the stationary gel. It is generally found that the mutual incompatibility of polymers increases rapidly with an increase of molecular weight.[32]

Dawkins[2] has given a more rigorous thermodynamic treatment of eq 16 than that he gave previously.[33] Dawkins[2] arrives at the following expression:

$$-\ln K_p = X_2\phi_3(1 + \chi_{23}) \qquad (19)$$

where K_p is the distribution coefficient for solute–gel interaction, X_2 is the degree of polymerization of the polymer, ϕ_3 is the volume fraction of the gel, and χ_{23} is the polymer–gel interaction parameter. To obtain eq 19, Dawkins[2] made some simplifications: the polymer separation is carried out in dilute solutions; the eluent is highly compatible with the polymer and the solvent for the gel, so that there exists athermal mixing, i.e., $\chi_{12} = \chi_{13} = 0$, where χ_{12} and χ_{13} are the solvent–polymer and solvent–gel interaction parameters, respectivey; X_3, the degree of polymerization of the gel, is taken as $X_3 = \infty$; ϕ_2, the volume fraction of the polymer, is taken as $\phi_2 = 0$, and consequently $\phi_3 = 1 - \phi_1$, etc.

Phenomena due to strong a polymer–gel interaction in a partition mechanism give rise to negative values of χ_{23}, whereas the incompatibility effect yields positive values of χ_{23}. Application of eq 19 to our experimental data gives the following results. In Figure 4 we show the values of K_p from Table I plotted as ln K_p vs. $\bar{X}_{2,n}$. We can see that the proportionality between ln K_p and X_2 predicted by eq 19 is approximately followed by our results in spite of the marked difference from sample to sample in the dependence of K_p (ln K_p) on molecular weight. This fact confirms the reliability of eq 16 and 18 for the purpose of determining K_p and hence the adequacy to explain the polymer separation involving steric exclusion and partial exclusion by incompatibility between PVK-3,6-Br$_2$ as solute and polystyrene network as gel. It also explains the adequacy of eq 19 to describe the dependence of K_p on molecular weight in spite of the simplification on which it has been based.

We have carried out phase separation experiments with PVK-3,6-Br$_2$ and linear PS in THF to ascertain the incompatibility between the polymers. The results are shown on Figure 1. We can see that miscibility is restricted when the two polymers are present in the solution, so that PVK-3,6-Br$_2$ and PS are in fact incompatible to a certain degree.

Incompatibility between polymers will correspond, in general, to a positive value of χ_{23}. However, phase separation in ternary systems can happen even when the two polymers are compatible ($\chi_{23} < 0$) if the affinities of the two polymers for the solvent are sufficiently different, that is, if the value of $|\chi_{12} - \chi_{13}|$ is large enough.[34] In our case, THF is a good solvent for both polymers and we do not expect a large value of $|\chi_{12} - \chi_{13}|$; therefore, the phase diagram of Figure 1 is taken as indication of a positive χ_{23}.

We can calculate the value of χ_{23} for PVK-3,6-Br$_2$ + PS at the plait point of the phase diagram of Figure 1, $(\chi_{23})_{pl}$. To calculate $(\chi_{23})_{pl}$ we follow Scott[35,36]

$$(\chi_{23})_{pl} = (1/2)(X_2^{-1/2} + X_3^{-1/2})(1 - \phi_{1,pl})^{-1} \qquad (20)$$

where X_2 and X_3 have the same meaning as above and $\phi_{1,pl}$ is the volume fraction of solvent taken at the plait point. From the phase diagram in Figure 1 and physical constants for THF, PVK-3,6-Br$_2$, and PS, given in the Experimental Section, we obtain $(\chi_{23})_{pl} = 0.0083$.

The values of the interaction parameters between polymers are in general very small, of an order similar to the value here found for $(\chi_{23})_{pl}$. Polymer–solvent interaction parameters are usually larger because they contain an entropic contribution (of the order 0.3–0.4) that is due to the dissimilarity in molecular size between the two components. Polymer–polymer interaction parameters, on the other hand, are much smaller because this entropic contribution, typical of polymer–solvent systems, disappears when both components are high polymers.

In the case of two polymers in the presence of a solvent, Van den Esker and Vrij[37] have calculated the interaction parameter, χ_{23}, using the Flory–Prigogine–Patterson[38–41] theory of polymer solutions. Their result is

$$\chi_{23} = \frac{p_1^* V_1^*}{RT\tilde{v}_1}\left\{(A_{12} - A_{13})^2\frac{\alpha_1 T}{2} + \frac{(\sigma_2 - \sigma_3)(\sigma_2 X_{12} - \sigma_3 X_{13})}{p_1^*} + \frac{\sigma_2\sigma_3 X_{23}}{p_1^*}\right\} \qquad (21)$$

$$A_{1j} = \frac{p_j^*}{p_1^*}\left(1 - \frac{T_1^*}{T_j^*}\right) - \frac{\sigma_j X_{1j}}{p_1^*} \qquad (22)$$

$$\sigma_i = S_i/S_1 \qquad (23)$$

Here p_i^*, V_i^*, and T_i^* are reduced parameters for pressure, volume, and temperature corresponding to component i, S_i is the molecular surface to volume ratio of said component, α_1 is the coefficient of thermal expansion of the solvent, $\tilde{v}_1$ is the solvent reduced volume, and the X_{ij}'s are exchange interaction parameters for the pair of components i and j. In the presence of a solvent, χ_{23} is not a purely binary parameter for polymers 2 and 3 because the solvent characteristics intervene also in determining χ_{23}, as given by eq 21. However, the first two terms in the right-hand side of eq 12 are differences that partially cancel, and the resulting χ_{23} is always small.

Incompatibility is then obtained even for small positive values of χ_{23} such as the $(\chi_{23})_{pl}$ found here for PVK-3,6-Br$_2$ + PS in THF. This raises a problem with regard to eq 19. The contribution of the interaction parameter χ_{23} to K_p in the factor $(1 + \chi_{23})$ appears to be of secondary importance because $\chi_{23} \ll 1$. Hence, it is difficult to understand how the incompatibility represented by χ_{23} can be made responsible for the results $K_p < 1$ and $-\ln K_p \sim X_2$. Even for a neutral pair of polymers ($\chi_{23} + 0$), K_p would be different from unity and $-\ln K_p$ an increasing function of X_2, according to eq 19.

In order to analyze this problem in more detail, we could go back to the original equations of Scott[35] for the chemical potentials of the three components in the ternary system and write the equilibrium conditions avoiding some of the simplifications introduced in the derivation of eq 19. Instead of doing this, we prefer an alternative though entirely equivalent procedure.

Selective Adsorption. We realize that the problem of the adsorption of the solute polymer onto the gel, or the opposite case of incompatibility between solute polymer and gel, can be viewed as a problem in preferential or selective sorption. Namely, the gel equilibrates with a binary mixture (solvent + solute polymer), the result being that the composition of the binary mixture (the concentration of the polymer) inside the gel differs from the composition outside. The balance of interactions between solvent (1), solute polymer (2), and gel (3) determines the amount of selective adsorption or desorption of polymer by the gel.

Thus viewed, we can use thermodynamics to write the equation for preferential sorption and apply it to the case of a gel phase in the presence of a binary liquid phase. According to Māša et al.,[42] the equation is

$$(\partial G_u/\partial u_1) = (\partial G_{u0}/\partial u_{10}) \tag{24}$$

where $u_i = \phi_i/(1 - \phi_3)$, the subscript zero means binary liquid phase outside the gel, and G_u is the Gibbs function of mixing per unit volume of liquid: $G_u = \Delta G_M/V(1 - \phi_3)$, with V being the total volume and ΔG_M the Gibbs function of mixing.

Using a Flory–Huggins model for ΔG_M

$$\Delta G_M = \sum_{i=1}^{3} n_i \ln \phi_1 + n_1\phi_2 g_{12} + n_1\phi_3 g_{13} + n_2\phi_3(V_2/V_1)g_{23} \tag{25}$$

where the g_{ij}'s are interaction parameters per segment or per molar volume of solvent (V_1), and substitution into equation 24 yields

$$\ln (\phi_2/\phi_{20}) = -(V_2/V_1)\phi_3\left[\phi_3^{-1} \ln (\phi_{10}/\phi_1) + g_{23} - g_{13} - g_{12}\left(1 + 2\frac{(\phi_2 - \phi_{20}}{\phi_3}\right)\right] \tag{26}$$

An equation entirely equivalent to this but with interaction parameters based on chemical potentials, χ_{ij}'s, instead of the g_{ij}'s was derived by Krigbaum and Carpenter[43] in their treatment of selective sorption and also by Sakurada et al.,[44] in their study of phase equilibria in ternary systems containing a solvent, a linear polymer, and a cross-linked polymer. The g_{ij}'s and χ_{ij}'s differ because of the dependence of interaction parameters on polymer concentration. They are related through

$$\chi_{ij} = g_{ij} - (1 - \phi_j)(\partial g_{ij}/\partial \phi_j) \tag{27}$$

Expanding $\ln (\phi_{10}/\phi_1)$ in eq 26 up to linear terms, we have

$$\ln (\phi_2/\phi_{20}) = -(V_2/V_1)\phi_3\left[1 + g_{23} - g_{12} - g_{13} + \frac{\phi_2 - \phi_{20}}{3}(1 - 2g_{12})\right] \tag{28}$$

and neglecting $\phi_2 - \phi_{20}$ terms, we arrive at

$$\ln (\phi_2/\phi_{20}) = -(V_2/V_1)\phi_3(1 + g_{23} - g_{12} - g_{13}) \tag{29}$$

The quotient (ϕ_2/ϕ_{20}) is the partition coefficient K_p calculated by Dawkins;[2] therefore, $\ln K_p = \ln (\phi_2/\phi_{20})$ can be equated to the right-hand side of eq 29

$$\ln K_p = -(V_2/V_1)\phi_3(1 + g_{23} - g_{12} - g_{13}) \tag{30}$$

This expression is more general than eq 19 in which the interaction parameters g_{12} and g_{13} are absent. In deriving eq 19 we took $\chi_{12} + \chi_{13} = 0$ on the assumption that athermal mixing takes place between the solvent and each one of the two polymers (solute and gel). But, as we have discussed above, even for athermal mixing there is an entropic contribution that brings each of the polymer–solvent interaction parameters χ_{12} and χ_{13} to the range 0.3–0.4. Usually, the interaction parameters are increasing functions of polymer concentration, so that $(\partial g_{12}/\partial \phi_2) > 0$ and $(\partial g_{13}/\partial \phi_0) > 0$. This gives according to eq 29 $g_{12} > \chi_{12}$ and $g_{13} > \chi_{13}$. Therefore, the term $-(g_{12} + g_{13})$ neglected in eq 19 can reach values similar to unity and give for $(1 - g_{12} - g_{13})$ values close to zero or of the same order of magnitude as g_{23}.

It is then necessary to consider the full eq 30 to understand how K_p can be unity or differ from unity depending on the balance of the interaction parameters $(1 + g_{23} - g_{12} - g_{13})$.

The molecular weight dependence of K_p predicted by eq 30 is the same as that of eq 19 since (V_2/V_1) is proportional to the degree of polymerization X_2. Although the molecular weight dependence of $\ln K_p$ is mainly given by this front factor X_2 in both eq 30 and 19, there is a residual dependence contained in the interaction parameter g_{23} or χ_{23}. As Strazielle[45] has shown, χ_{23} for two polymers in solvent depends on the molecular weights, M_2 and M_3, of the polymers.

Kratochvíl and Vorlícek[46] have derived an expression for the selective sorption of polymer 2 by polymer 3 in dilute solution $(\partial C_2/\partial C_3)_{C_3 \to 0}$, where C_i is the concentration of polymer. Positive values of $(\partial C_2/\partial C_3)_{C_3 \to 0}$ represent adsorption of polymer 2 by polymer 3, and negative values represent selective exclusion of polymer 2 from 3 or incompatibility. Kratochvíl et al.[46–49] have used light scattering to determine the interaction between two polymers in solution. Their results correspond to negative $(\partial C_2/\partial C_3)_{C_3 \to 0}$ in a number of systems, that is, to selective exclusion or desorption of polymer 2 by polymer 3. Campos and Strazielle[50] have measured $(\partial C_2/\partial C_3)_{C_3 \to 0}$ in the system benzene (1) + poly(dimethylsiloxane) (2) + polystyrene (3) and have found negative $(\partial C_2/\partial C_3)_{C_3 \to 0}$ and the values of $-(\partial C_2/\partial C_3)_{C_3 \to 0}$ increasing with the molecular weight of 2.

The aim of the above discussion has been to show that both the experimental finding as well as the theoretical predictions in the field of selective sorption in ternary systems composed by two polymers and a solvent are related to and can be used to interpret the problems arising from incompatibility and deviations from universal calibration in GPC. As expressed by eq 30, the deviations from universal calibrations ($K_p \neq 1$) should be in general dependent on all three interaction parameters of the system (g_{23}, g_{12}, g_{13}) and not just on incompatibility ($g_{23} \neq 0$).

Gel Volume. The slope of the plot $\ln K_p$ vs. X_2 of Figure 4 gives the value 4.3×10^{-4}. From this value we could calculate the gel volume fraction, ϕ_3, if all the interaction parameters g_{12}, g_{13}, and g_{23} were known. However, we can make a rough estimate by assuming that the balance $(1 + g_{23} - g_{12} - g_{13})$ lies in the approximate range

0.01–0.02. Then $0.002 < \phi_3 < 0.04$. This magnitude of ϕ_3 can throw some light, at least from a qualitative point of view, on the structure of the gels. According to these limit values, ϕ_3 is quite small and therefore only a fraction of the cross-linked solvated stationary phase is taking part in the separation process. All this may be consistent with a model of a macroporous gel with decreasing concentration of the polymer solution toward the center of the pores.[51]

Specific Effects. Let us focus now on the possible influence of the specific structural effects of PVK-3,6-Br_2 on its GPC behavior as a cause for the deviations from universal calibration reported here. The repeating unit of PVK-3,6-Br_2 contains a nitrogen atom carrying a lone electron pair and it also contains two bromine atoms on the carbazolyl ring. It has been found previously that the homologous polymer PVK, which also carries a *N*-carbazolyl ring in its repeating unit, falls on the same hydrodynamic volume plot as PS with THF as eluent.[52] So, the discrepancies here reported can be attributed to the two bromine atoms attached to the ring at the 3 and 6 positions. These bulky substituents give rise to an increased incompatibility or larger selective desorption of the polymer by the gel.

From another point of view, Ouano et al.[53] suggested that the usually low GPC retention characteristics of poly(bicycloheptyl sulfone) in chloroform ($CHCl_3$), in relation to its true molecular weight (as determined by light scattering), may be explained because the PBCHS strongly associates with $CHCl_3$ solvent perhaps through hydrogen bonding. The increase in the apparent heterogeneity index and the tailing of the low molecular weight fraction of PBCHS may be explained also by the same phenomena; i.e., strong solvent interaction can result in lower permeation into the stationary phase, hence lower retention volumes.

Both polymers, PVK-3,6-Br_2 and PBCHS, present high values for their respective Mark–Houwink exponents in the solvent employed in GPC experiments for each of them. Thus the Mark–Houwink relationships are respectively[13,53] as follows:

$$\text{PVK-3,6-Br}_2 \qquad [\eta]\ (\text{mL/g}) = 1.27 \times 10^{-3} M^{0.80} \qquad 25\ ^\circ\text{C and THF}$$

$$\text{PBCHS} \qquad [\eta]\ (\text{mL/g}) = 1.58 \times 10^{-3} M^{0.79} \qquad 25\ ^\circ\text{C and CHCl}_3$$

As Ouano et al.[53] have pointed out, the same behavior has been observed with other polymers containing highly polar groups, such as polyols.[54]

The difference of solvation between compounds of similar size and shape may be an element in their separation.[55,56] Horta[57] has given a theoretical prediction on the influence of the solvation on the fractionation of polymers by GPC. However, the solvation alone can not be the explanation to all the incompatibility processes observed in the literature. It contributes to a higher efficiency to the GPC when is considered as a separation technique.

Acknowledgment. A portion of the experimental work on which the present paper is partially based was done by J.M.B.R. at the Centre de Recherches sur les Macromolecules (CNRS, Strasbourg, France). J.M.B.R. gratefully acknowledges Dr. H. Benoît for his kind hospitality and fruitful conversations. Thanks are also given to Ministry for External Affairs of France for a fellowship to J.M.B.R. He also thanks Dr. Z. Grübisic-Gallot of the same Institute, who gave him advice on the techniques of GPC and made her laboratory facilities available to him and Michael Jacob for his help and advice with some of the experimental work but especially with that concerning the GPC technique experimentally considered. This work was in part supported by the Comision Asesora de Investigación Científica of the Ministerio de Educación y Ciencia through Grants-in-Aid for Scientific Research 3363/79 and 0077/81.

Registry No. PVK-3,6-Br_2 (homopolymer), 27599-53-7; PS (homopolymer), 9003-53-6; THF, 109-99-9.

References and Notes

(1) Dubin, P. L.; Koontz, S.; Wright, K. L., III *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2047.
(2) Dawkins, J. V. *Polymer* **1978**, *19*, 705.
(3) Dawkins, J. V. *Pure Appl. Chem.* **1979**, *51*, 1473.
(4) Audebert, R. *Polymer* **1979**, *20*, 1561.
(5) Dawkins, J. V. *J. Liq. Chromatogr.* **1978**, *1*, 279.
(6) Grübisic-Gallot, Z.; Rempp, P.; Benoît, H. *J. Polym. Sci., Part B* **1967**, *5*, 753.
(7) Benoît, H.; Grübisic-Gallot, Z.; Rempp, P.; Decker, D.; Zilliox, J. *J. Chim. Phys. Phys.-Chim. Biol.* **1966**, *63*, 1507.
(8) Dawkins, J. V.; Hemming, M. *Makromol. Chem.* **1975**, *176*, 1777.
(9) Heller, J.; Moacanin, J. *J. Polym. Sci., Part B* **1968**, *6*, 595.
(10) Dawkins, J. V., quoted by: Bevington, J. C.; Dyball, C. J. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1819.
(11) Mencer, H. J.; Grübisic-Gallot, Z. *J. Liq. Chromatogr.* **1979**, *2*, 649.
(12) Galera-Gômez, P. A.; Barrales-Rienda, J. M.; Otero Aenlle, E. *An. Quím., Ser. C* **1980**, *76*, 357.
(13) Barrales-Rienda, J. M.; Galera-Gômez, P. A. *Eur. Polym. J.* **1984**, *12*, 1213.
(14) Horta, A.; Sâiz, E.; Barrales-Rienda, J. M.; Galera-Gômez, P. A. *Polymer*, accepted for publication.
(15) Barrales-Rienda, J. M.; Romera Galicia, C.; Horta, A. *Macromolecules* **1983**, *16*, 932.
(16) Coll, H.; Gilding, D. K. *J. Polym. Sci., Part A-2* **1970**, *8*, 89.
(17) Papazian, L. A. *Polymer* **1969**, *10*, 399.
(18) Barrales-Rienda, J. M.; Galera Gômez, P. A.; Gonzalez Ramos, J.; Otero Aenlle, E. *An. Quím., Ser. C* **1980**, *76*, 49.
(19) Matheson, M. S.; Auer, E. E.; Bevilacqua, E. B.; Hart, E. J. *J. Am. Chem. Soc.* **1951**, *73*, 1700.
(20) Metz, D. J.; Glines, A. *J. Phys. Chem.* **1967**, *71*, 1158.
(21) Elias, H.-G.; Bareiss, R.; Watterson, J. G. *Adv. Polym. Sci.* **1973**, *11*, 111.
(22) Spatorico, A. L.; Coulter, B. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 1139.
(23) Lecourtier, J.; Audebert, R.; Quivoron, C. *Pure Appl. Chem.* **1979**, *51*, 1483.
(24) Klein, J.; Treichel, K. *Chromatographia*, **1977**, *10*, 604.
(25) Altgelt, K. H.; Moore, J. C. in "Polymer Fractionation"; Cantow, M. J. R., Ed.; Academic Press: New York, **1967**; p 145.
(26) Altgelt, K. H. *Makromol. Chem.* **1965**, *88*, 75.
(27) Altgelt, K. H. *Sep. Sci.* **1970**, *5*, 777.
(28) Ogston, A. G.; Silpananta, P. *Biochem. J.* **1970**, *116*, 171.
(29) Belenkii, B. G.; Vilenchik, L. Z.; Nesterov, V. V.; Kolegov, V. J.; Frenkel, S. Y. *J. Chromatogr.* **1975**, *109*, 233.
(30) Dawkins, J. V.; Hemming, M. *Makromol. Chem.* **1975**, *176*, 1795.
(31) Anderson, D. M. W.; Stoddart, J. F. *Anal. Chim. Acta* **1966**, *34*, 401.
(32) Morawetz, H. "Macromolecules in Solution", 2nd ed., Wiley: New York, 1975; p 91.
(33) Dawkins, J. V. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 569.
(34) Robard, A.; Patterson, D.; Delmas, G. *Macromolecules*, **1977**, *10*, 706.
(35) Scott, R. L. *J. Chem. Phys.* **1949**, *17*, 279.
(36) Krause, S. *J. Macromol. Sci., Rev. Macromol. Chem.* **1972**, *C7*, 251.
(37) Van den Esker, M. W. J.; Vrij, A. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1943.
(38) Flory, P. J.; Orwoll, R. A.; Vrij, A. *J. Am. Chem. Soc.* **1964**, *86*, 3507.
(39) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2035.
(40) Prigogine, I. "The Molecular Theory of Solutions"; North Holland: Amsterdam, 1957.
(41) Patterson, D. *J. Polym. Sci., Part C* **1968**, *16*, 3379.
(42) Mâsâ, Z.; Pouchlý, J.; Přibilovâ, J.; Biroš, J. *J. Polym. Sci., Polym. Symp.* **1975**, *53*, 271.
(43) Krigbaum, W. R.; Carpenter, D. K. *J. Polym. Sci.* **1954**, *14*, 241.
(44) Sakurada, I.; Nakajima, A.; Aoki, H. *J. Polym. Sci.* **1959**, *35*, 507.

(45) Strazielle, C. *Eur. Polym. J.* **1979**, *15*, 55.
(46) Kratochvíl, P.; Vorlíček, J. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1561.
(47) Kratochvíl, P.; Vorlíček, J.; Strakova, D.; Tuzar, Z. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 2321.
(48) Kratochvíl, P.; Straková, D.; Tuzar, Z. *Br. Polym. J.* **1977**, *9*, 217.
(49) Kratochvíl, P.; Straková, D.; Podešva, J. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 945.
(50) Campos, A.; Strazielle, C. *Eur. Polym. J.* **1978**, *14*, 517.
(51) Heitz, W.; Kern, W. *Angew. Makromol. Chem.* **1967**, *1*, 150.
(52) Sitaramaiah, G.; Jacobs, D. *Polymer*, **1970**, *11*, 165.
(53) Ouano, A. C.; Gipstein, E.; Kaye, W.; Dawson, B. *Macromolecules* **1975**, *8*, 558.
(54) Cazes, J.; Gaskill, D. R. *Sep. Sci.* **1969**, *4*, 15.
(55) Cazes, J.; Gaskill, D. R. *Sep. Sci.* **1967**, *2*, 421.
(56) Cazes, J.; Herron, S. *Sep. Sci.* **1973**, *8*, 395.
(57) Horta, A. *J. Macromol. Sci., Chem.* **1971**, *5*, 487.

Conformational Characteristics of Poly(2-vinylpyridine)

A. E. Tonelli

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received May 10, 1985*

ABSTRACT: Conformational energy calculations were coupled with dipole moment measurements to derive a conformational description of poly(2-vinylpyridine) (P2VP). When a rotational isomeric states (RIS) model was used to calculate the dipole moments of P2VP chains with different stereosequences, it was found that the calculated dipole moments were nearly independent of P2VP stereosequence. Dipole moments measured for three P2VP samples with very different stereosequences, as determined by ^{13}C NMR spectroscopy, were also very similar with magnitudes that agreed with the calculated dipole moments. In addition, the isomer fractions observed by Hogen-Esch et al. after the equilibrium epimerization of P2VP oligomers are also successfully reproduced by the RIS model developed here for P2VP.

Introduction

It has been observed[1–8] that vinyl polymers possessing large, planar side groups are limited in their conformational freedom. Previous studies of such vinyl polymers, i.e., poly(methyl methacrylate),[1,2] poly(methyl acrylate),[3] poly(vinyl acetate),[4] polystyrene,[5] poly(α-methylstyrene),[6] poly(*N*-vinylcarbazole),[7] and poly(*N*-vinylpyrrolidone),[8] led to the observation that the planarity of the side groups severely limits the conformations (ϕ_1,ϕ_2) available to the pair of backbone bonds flanked by these large, rigid side groups (see Figure 1). Poly(2-vinylpyridine) (P2VP) is another example of a vinyl polymer with planar side groups.

The pyridine side groups in P2VP are polar (see Figure 1) and may interact with each other in certain backbone conformations, such as the tt conformation of the meso (m) P2VP diad illustrated in Figure 1. In this conformation access of the backbone to solvent molecules is limited, a situation that also arises in the tg$^-$ conformation of a racemic (r) P2VP diad. Thus, we might expect the conformations adopted by the P2VP backbone to depend not only on stereosequence but also on solvent interactions and side-group orientations.

We have studied the conformational characteristics of P2VP chains by employing approximate potential energy functions to estimate their conformational energies. In addition to treating P2VP chains of different stereoregularity, side groups were permitted to adopt different orientations and solvent interaction energies were approximated. A rotational isomeric states (RIS) model was derived for P2VP from the conformational energy estimates. Mean-square unperturbed dimensions (end-to-end chain lengths) and dipole moments were calculated as a function of stereoregularity from the RIS model derived here for P2VP and were compared to dilute solution dimensions reported in the literature and to the dipole moments measured in the present study for three P2VP samples with different stereosequences.

Conformational Energies

Method of Calculation. The recently reported[9] crystal structure of 2,4,6,8-tetramethyl-2,4,6,8-tetra-2-pyridylnonane provides us with geometric information concerning the side groups in P2VP. The pyridine rings are planar and are very similar to phenyl rings in their geometry. As an example, the pyridine ring bond lengths and valence angles span the ranges 1.34–1.41 Å and 117–124°, while 1.39 Å and 120° are found[10] for phenyl rings. Consequently, we have used the geometrical parameters employed by Yoon et al.[5] in their treatment of polystyrene to calculate the conformational energies of P2VP.

Rotation about each backbone C–C bond was assigned a threefold intrinsic torsional potential with a barrier height of 2.8 kcal/mol. A Lennard-Jones 6–12 potential together with a Coulombic term were used to evaluate the nonbonded van der Waals and electrostic interactions between atoms. Parameters of the 6–12 potential were the same as those employed by Yoon et al.[5] for polystyrene and by us[8] for poly(*N*-vinylpyrrolidone). From the dipole moment measured[11] for pyridine in dilute solutions (2.25 D), partial charges of −0.68 and +0.34 were assigned respectively to the N atom and the two C atoms bonded to it, and a dielectric constant of 3.5 was assumed to mediate the electrostatic interactions.

Certain conformations of vinyl polymers with large side-chain substituents can prevent solvent molecules from gaining access to the polymer backbone (see Figure 1). However, for an m diad in the tg$^-$ conformation the side chains are sufficiently separated to permit access of the solvent. By replacing side-chain–side-chain interactions with side-chain–solvent interactions when the the distance r between side chains becomes sufficiently great ($r = \sigma$), Yoon et al.[5] devised a procedure to account for the conformational dependence of solvent interactions. The energy of interaction should level off at the distance σ, and we therefore require the calculated conformational energy to remain constant at its value for $r = \sigma$ for all distances greater than σ. Judging from previous results[1–8] σ = 4–5 Å seems reasonable, and we have employed σ = 4.5 Å and ∞ (no solvent–polymer interactions considered) in our calculations on P2VP.

Backbone rotation angles ϕ_1 and ϕ_2 were stepped in 10° increments and were measured in a right-handed sense (a different rotation angle sign convention was employed in