

On the Selectivity of Adsorption Chromatography

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SYNOPSIS

In this paper, the shape of chromatograms obtained by elution of copolymers with a mixture of solvent–nonsolvent of variable composition has been studied from a theoretical point of view. It is assumed that the thermodynamic quality of the mixture at which the copolymer is eluted depends only on its composition and not on its mass and structure. If one characterizes the polydispersity in composition, assuming that each constituent obeys a molar mass distribution of the Zimm–Schulz type, one can draw the following curves: concentration of the copolymer versus eluant composition. They depend on three parameters, including composition of the copolymer and the polydispersity of each constituent. The most striking result is that the shape of the chromatogram changes dramatically when one increases the polydispersity of either constituents. For low polydispersities, one obtains a classical peak. For large polydispersities, the chromatogram has a minimum for the intermediate values of composition and presents peaks in the vicinity of the pure homopolymers. This can be explained easily by a qualitative argument. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

During the last few years, efforts have been made in the field of polymer science to replace or complement the classical size exclusion chromatography (SEC) by adsorption chromatography.^{1–4} While size exclusion chromatography selects the molecules by their size, it is not sensitive to composition. This makes, for instance, in the case of a mixture of homo and copolymers, fractionation as a function of the composition impossible, even if one has at his disposal many types of detectors. This explains why people have tried to develop adsorption chromatography that is very sensitive to the chemical nature of the species under study and much less on molar mass. One of the major difficulties of this technique is that, if one does not take any precaution, it is sensitive to all the parameters defining the structure of the molecules in the case of copolymers, including, degree of polymerization (DP) of each constituent, number of blocks of each species, and spatial distribution of the blocks. Recent progress has shown

that, by a judicious choice of the experimental conditions, one can obtain working conditions for which the elution time is only sensitive to composition and therefore independent of degree of polymerization and structure.⁵

In this paper, we would like to report a theoretical study on the kind of information one obtains by this technique. We shall assume, therefore, that we have at our disposal a chromatographic instrument in which we use a mixture of a precipitant as solvent. A good solvent, the composition of this mixture, which starts from the nonsolvent and goes continuously to a good solvent, is measured and registered. A preliminary calibration allows the establishment of a relation between the composition (ϕ) of the solvent mixture, for which the copolymer is eluted to its composition (ϕ_0). A chromatogram is therefore a diagram showing the composition of the elute polymer as a function of its composition ϕ_0 .

In this paper, we shall use as an example the case of a copolymer made of two different monomers, a and b. The parts a and b have as degree of polymerization (DP) n_a and n_b , respectively. The composition is defined as $\phi_a = n_a/(n_a + n_b) = 1 - \phi_b$. If the part a of the copolymer, as well as part b, are monodisperse, and if the chromatographic device is

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perfect (in the sense of total selectivity), one should obtain a sharp peak that can be represented by a delta function. Practically, when both a and b parts are polydisperse, the composition of the copolymer is not constant, and this introduces a broadening of the peak. The purpose of this paper is to evaluate this broadening for different experimental conditions. In order to specify the experimental conditions, we can consider a copolymer made of two blocks; but since we assume that the chromatogram depends only on the composition and not on the structure, this does not modify the generality of the results, which should be valid for any kind of copolymer.

THE GENERAL EQUATION

We introduce the probability $w_{ab}(n_a, n_b) dn_a dn_b$ of finding one molecule having part a of the DP comprised between n_a and $n_a + dn_a$, and comprised between n_b and $n_b + dn_b$ for part b.

The quantity $w_{ab}(n_a, n_b) dn_a dn_b$ is expressed in the number of molecules. If one calls ν the total number of molecules and $d\nu$ the number of them having a DP comprised between n_a and $n_a + dn_a$, n_b and $n_b + dn_b$, one obtains

$$\frac{d\nu}{\nu} = w_{ab}(n_a, n_b) dn_a dn_b \quad (1)$$

If one assumes that the composition in a monomers and b monomers are statistically independent, one can write

$$w_{ab}(n_a, n_b) = w_a(n_a)w_b(n_b) \quad (1a)$$

where $w_a(n_a)$ and $w_b(n_b)$ are normalized as follows: $\int_0^\infty w_a(n_a) dn_a = \int_0^\infty w_b(n_b) dn_b = 1$. In order to determine the number of molecules having a given composition, $x = n_a/n_b$, one introduces the improper

Dirac delta function $\delta\left(\frac{n_a}{n_b} - x\right)$ of the variable x ($x \geq 0$), which is equal to zero if $x \neq n_a/n_b$ and which gives 1 after integration over x from 0 to infinity. Thus, the probability for a copolymer molecule to have the composition x and n_a and n_b monomers of nature a and b is given by

$$w(n_a, n_b, x) dn_a dn_b dx = w_a(n_a)w_b(n_b)\delta\left(\frac{n_a}{n_b} - x\right) dn_a dn_b \quad (2)$$

Since we assume that our detector is sensitive to the concentration and not to the number of molecules we have to multiply by $(n_a + n_b)$ in order to go from the number of molecules to the mass of polymer, obtaining the quantity we call dc ,

$$dc = (n_a + n_b)w(n_a, n_b, x) dn_a dn_b dx = w_a(n_a)w_b(n_b)\delta\left(\frac{n_a}{n_b} - x\right) \times (n_a + n_b) dn_a dn_b \quad (3)$$

It is important to note that the concentration c is not normalized to unity but obeys the relation

$$\iint_{n_a n_b} dc = \bar{n}_a + \bar{n}_b \quad (4)$$

where \bar{n}_a and \bar{n}_b are the number-average degrees of polymerization of parts a and b, respectively.

Now we just have to integrate over n_a and n_b at constant x in order to obtain the concentration c of polymer for the composition x . This is done by replacing n_a with the new variable $u = n_a/n_b$, obtaining

$$c(x, n_b) = \int_{n_b=0}^{\infty} n_b^2 w_b(n_b) \left[\int_{u=0}^{\infty} (1+u) w_a(un_b) \times \delta(u-x) du \right] dn_b \quad (5)$$

Integrating, first on u and then on n_b , gives

$$c(x) = \int_0^\infty w_b(n_b) w_a(xn_b) (1+x) n_b^2 dn_b \quad (6)$$

If one wants to have a function $\gamma(x)$ normalized to unity, it suffices, following eq. (4), to write

$$\gamma(x) = \frac{c(x)}{\bar{n}_a + \bar{n}_b} = \frac{1}{\bar{n}_a + \bar{n}_b} \int_0^\infty w_b(n_b) w_a(xn_b) \times (1+x) n_b^2 dn_b \quad (7)$$

THE CASE OF THE SCHULTZ-ZIMM DISTRIBUTION

The General Equation

In order to be able to see the meaning of this result, it is important to take an example for which numerical calculations are possible. This is the case of the well-known Schultz-Zimm^{6,7} distribution, which

we shall use now. This distribution is described by the equation

$$w(n) dn = \frac{k^k}{\Gamma(k)} \left(\frac{n}{\bar{n}}\right)^{k-1} \exp\left(-k \frac{n}{\bar{n}}\right) \frac{dn}{\bar{n}} \quad (8)$$

where $\Gamma(k)$ is the gamma function of the argument k , ($\Gamma(k) = (k-1)!$ for k integer), \bar{n} is the number average DP, and $k(k > 0)$ is a parameter defining the polydispersity of the sample. Calling \bar{n}_w the weight-average degree of polymerization, one defines k by the following relation:

$$\frac{\bar{n}_w}{\bar{n}_n} = 1 + \frac{1}{k} \quad (9)$$

When $k = 1$, one has the most probable distribution, (\bar{n}_w/\bar{n}_n) = 2. For $k \rightarrow \infty$, the distribution is narrow and broadens when k decreases. Using this definition of $w(n)$ and replacing \bar{n}_a by a , \bar{n}_b by b , and the variable n_b by n , eq. (7) becomes, assuming that the two polymers are different,

$$\begin{aligned} \gamma(x) = & \frac{1}{a+b} \int_{n=0}^{\infty} dn \frac{n^2}{ab} \left[\frac{k^k}{\Gamma(k)} \left(\frac{n}{b}\right)^{k-1} \right. \\ & \times \exp\left(-k \frac{n}{b}\right) \frac{k'^{k'}}{\Gamma(k')} \left(\frac{xn}{a}\right)^{k'-1} \\ & \left. \times (1+x) \exp\left(-k' \frac{xn}{a}\right) \right] \quad (10) \end{aligned}$$

The Blocks Have the Same DP and the Same Polydispersity

In a first approach, we simplify the problem, assuming that the polymers a and b are identical (they have the same number-average DP ($a = b$) and the same polydispersity ($k = k'$). Defining $n/a = n/b = u$, eq. (10) becomes

$$\begin{aligned} \gamma(x) = & \frac{1}{2} \left[\frac{k^k}{\Gamma(k)} \right]^2 x^{k-1} (1+x) \\ & \times \int_{u=0}^{\infty} \exp\{-k(1+x)u\} (u^{2k}) du \quad (11) \end{aligned}$$

As expected, it does not depend on molar mass and is easy to integrate using as variable $z = k(1+x)$, as follows:

$$\begin{aligned} \gamma(x) = & \frac{k^{2k}}{[\Gamma(k)]^2} \frac{(1+x)}{2} x^{k-1} \left[\frac{1}{k(1+x)} \right]^{2k+1} \\ & \times \int_{z=0}^{\infty} dz [z^{2k} \exp(-z)] \quad (12) \end{aligned}$$

The integral is equal to $\Gamma(2k)$, and one obtains

$$\gamma(x) = \frac{\Gamma(2k)}{[\Gamma(k)]^2} \frac{x^{k-1}}{(1+x)^{2k}} \quad (13)$$

$\gamma(x)$ is normalized to unity $\int_{x=0}^{\infty} \gamma(x) dx = 1$; it is the relative weight in the mixture of the copolymer having a given value of $x = n_a/n_b$. It is more convenient and nearer to the experiments to use as a variable, instead of x , the composition $\phi_a = n_a/(n_a + n_b) = \frac{x}{1+x}$ ($0 < \phi_a < 1$). Using this new variable allows us to write γ as a function of ϕ_a in order to have $\gamma(x) dx = \gamma(\phi_a) d\phi_a$. This gives, after simple calculations,

$$\begin{aligned} \gamma(\phi_a) d\phi_a = & \gamma(x) dx \\ = & \frac{\Gamma(2k)}{[\Gamma(k)]^2} [\phi_a(1-\phi_a)]^{k-1} d\phi_a \quad (14) \end{aligned}$$

The result is, as it should be, perfectly symmetrical.

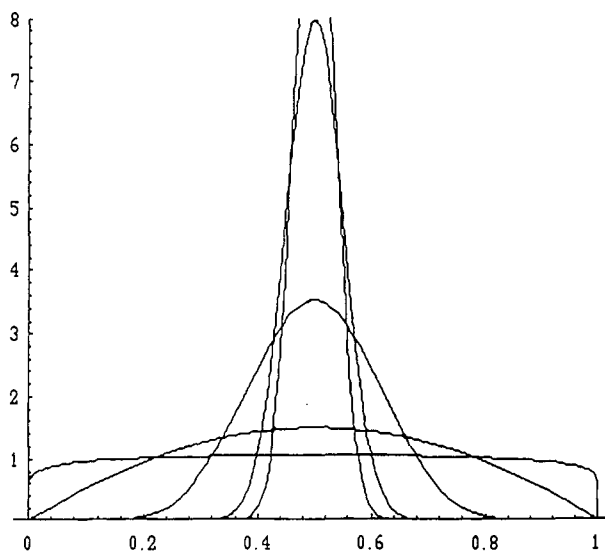


Figure 1 $\gamma(\phi)$, reduced concentration as a function of the composition ϕ . $n_w/n_n = 1.01, 1.02, 1.1, 1.5,$ and 1.95 (top to bottom).

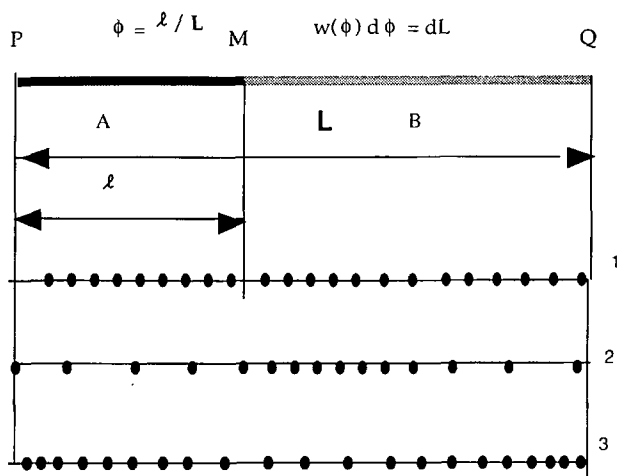


Figure 2 Schematic diagram showing how one can build up a distribution with the constant $\gamma(\phi)$.

Discussion of the Results for a Copolymer Made of Two Blocks Having the Same Polydispersity

$k > 1$

In Figure 1, curves corresponding to different values of k have been drawn. The results are remarkably simple. As expected, all the curves have a maximum for $\phi = 0.5$, the average composition of the copolymer.

The peak becomes narrower when k increases (i.e., the polydispersity decreases). The most remarkable feature is that for $k = 1$ ($n_w/n_n = 2$), there is a drastic change in the shape of the curves.

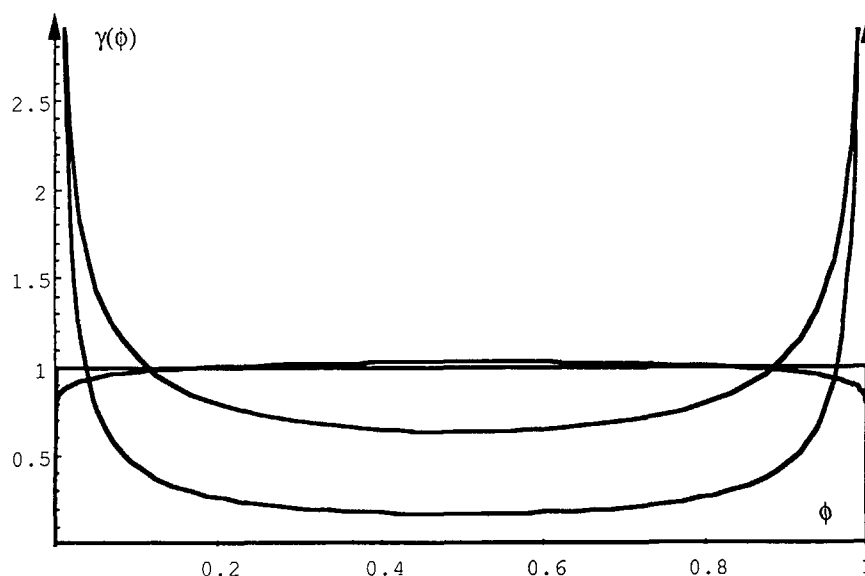


Figure 3 The function $\gamma(\phi)$ (normalized to unity) for systems with large polydispersity. Going from the top to the bottom at $\phi = 0.5$, one meets the curves corresponding to $n_w/n_n = 1.95, 1.995, 3, \text{ and } 11$.

For this value of k , each sequence obeys the most probable distribution, and we find $\gamma(\phi_a) = 1$ for all values of ϕ_a . The chromatogram is reduced to a horizontal straight line. This unexpected result needs a qualitative explanation.

A Qualitative Explanation for the Case $k = 1$

Let us take a linear chain of length L (Fig. 2) and cut it in two parts at an arbitrary point M , of abscissa ℓ , randomly chosen. The left part will be considered as an A chain of length ℓ ; the right as a B chain of length $L - \ell$. The composition of one molecule will be $\phi_a = \ell/L$, and the probability for having this composition will be $d\ell/L$, since all points have the same probability. This gives a chromatogram, which is the horizontal line, theoretically predicted for the most probable distribution ($k = 1$). This case does not correspond exactly to our model since $w_a(n_a)$ is not independent of $w_b(n_b)$ and eq. 1 (a) is not valid. It gives for the straight line $M_w/M_n = 1.33$ instead of 2. This shows that the result depends on the hypothesis that has been utilized to describe the polydispersity.

The Case $k \leq 1$ (Large Polydispersity)

If we continue to increase the polydispersity, the shape of the chromatogram changes drastically, and Figure 3 shows the result for $\gamma(\phi)$ as function of ϕ for different values of k .

Going from the top to the bottom at $\phi = 0.5$, one meets the curves corresponding to $n_w/n_n = 1.95, 1.995, 3, \text{ and } 11$.

In this region ($0 < k < 1$), the chromatograms are very special and show what we could call two peaks, one at $\phi = 0$, corresponding to pure homopolymer a, and the other at $\phi = 1$, corresponding to homopolymer b. It is justified to call these maxima peaks since one has to recover the baseline when one gets experimental compositions that are out of the interval $0 < x < 1$. This type of shape is easily explained if one goes back to Figure 2. We have seen that, if the point M has the same probability everywhere along the segment PQ, the chromatogram reduces to an horizontal straight line. In order to reduce the polydispersity, one has to have more points on the central part of the segment PQ or, in other words, a function $\gamma(\phi_a)$ corresponding to Figure 1. If the polydispersity is larger, then one must have more points corresponding to large differences from the average composition ($\phi = 0.5$); that is, in the vicinity of P and Q, this gives to the curves the shape that is observed on Figure 3 for $x > 2$.

This result is quite different from what is observed in exclusion chromatography; and, if an experimentalist has no theoretical a priori, he could easily misinterpret the data and conclude that the mixture is composed of two homopolymers pure a and pure b, which is wrong.

The fact that in adsorption chromatography, a broad monomodal distribution leads to a chromatogram with two peaks is unexpected and is one of the differences between this technique and S.E.C., it should be verified experimentally.

The General Case

In order to simplify the discussion, we have, until now, considered only the case in which the two sections of the copolymer are identical in length ($\phi = 0.5$) and in which the polydispersity of both constituents is the same. In order to draw the curves corresponding to other situations for which neither the length or the polydispersity is identical, we have to generalize eq. (14). We do not intend to discuss the case in which the chromatograms have more than one peak since, knowing what happens with a monomodal distribution, one can extrapolate the results to a multimodal one. Rather, we want to see if some important changes can be foreseen when one studies copolymers of very asymmetric composition or with very different polydispersities. For this purpose, we still use the Zimm-Schultz distribution. Equation (10) is valid for different polydis-

persities characterized by k for the monomer a and k' for monomer b and different DPs. Using as a parameter the quantity $y = a/b$ and as a variable the quantity $z = n/b \left(k + k' \frac{x}{y} \right)$, we can write it as follows:

$$\gamma(x) = \frac{k^k}{\Gamma(k)} \frac{k'^{k'}}{\Gamma(k')} \frac{1+x}{1+y} \frac{x^{k'-1}}{y^{k'}} \frac{1}{\left[k + k' \frac{x}{y} \right]^{k+k'+1}} \times \int_{z=0}^{\infty} dz [z^{k+k'} \exp(-z)] \quad (15)$$

The integral is the gamma function of $k + k' + 1$, $\Gamma(k + k' + 1)$, and we write

$$\gamma(x) = k^k k'^{k'} \frac{\Gamma(k + k' + 1)}{\Gamma(k)\Gamma(k')} \frac{1+x}{1+y} \times \frac{x^{k'-1} y^{k+1}}{(yk + xk')^{k+k'+1}} \quad (16)$$

If, as we did already, we use the volume fraction $\phi = \phi_a$ as variable and the quantity $\phi_0 = \frac{a}{a+b}$, which is the volume fraction occupied by the part a of the copolymer as parameter, we obtain the following:

$$\gamma(\phi) = \frac{\Gamma(k + k' + 1)}{\Gamma(k)\Gamma(k')} \times \frac{k^k k'^{k'} \phi^{k'-1} (1-\phi)^{k-1} \phi_a^{k+1} (1-\phi_0)^{k'+1}}{[k\phi(1-\phi_0) + k'\phi_0(1-\phi)]^{k+k'+1}} \quad (17)$$

This equation describes all configurations in which the polydispersity of the blocks is represented by the Schultz-Zimm distribution. In such a short note, it is impossible to discuss all the cases, and we shall study only two cases: (a) the two blocks have the same number average molar mass but different polydispersities; and (b) the molar masses are different, but the polydispersity is the same (Fig. 4).

Case of a Copolymer Having Two Blocks of Equal Number Average Length but Different Polydispersity

It suffices to simplify eq. (17) by writing $y = 1$ or $\phi_0 = \frac{1}{2}$ (the number average molar mass of both sequences are identical), obtaining

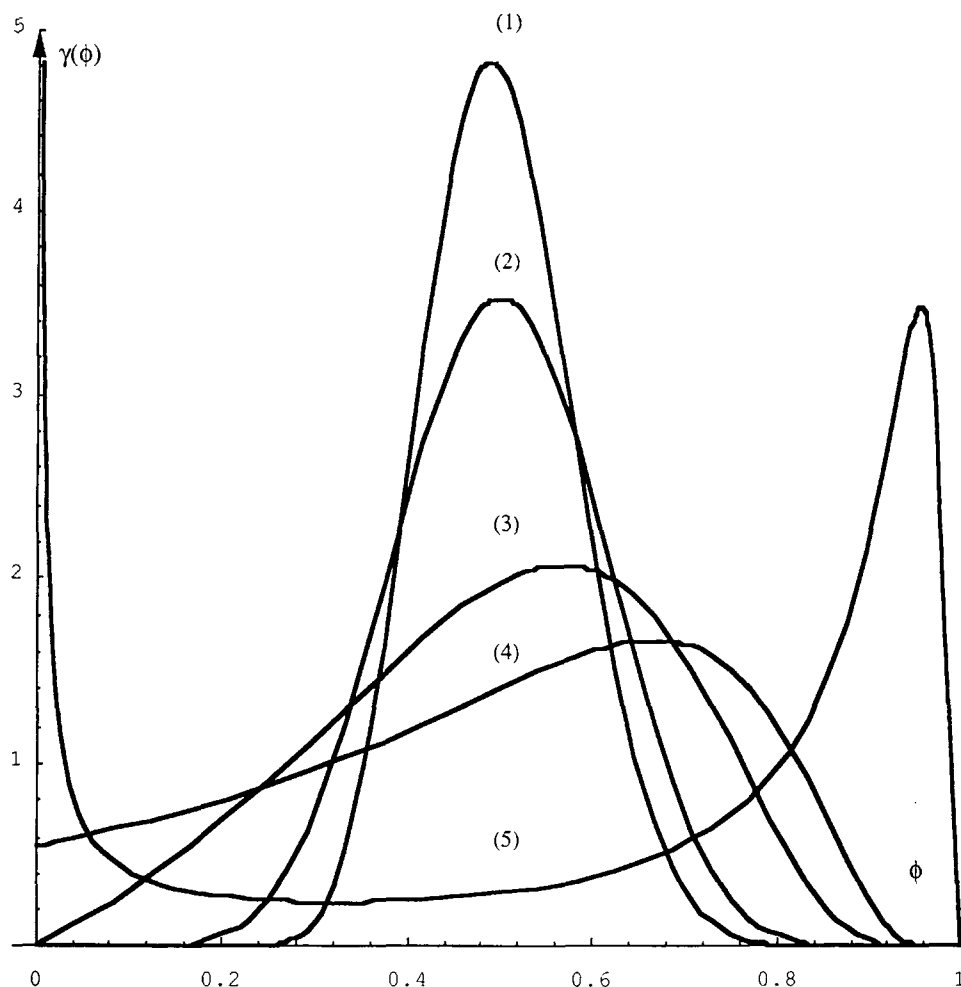


Figure 4 The function $\gamma(\phi)$ for $n_{wa}/n_{na} = 1.1$ and different values of the polydispersity of the block b: curve (1) $n_{wb}/n_{nb} = 1.01$; (2) $n_w/n_n = 1.1$; (3) $n_w/n_n = 1.5$; (4) $n_w/n_n = 2$; (5) $n_w/n_n = 11$.

$$\gamma(\phi) = \frac{k^k k'^{k'} \Gamma(k + k' + 1)}{2k[\Gamma(k)]\Gamma(k')} \frac{\phi^{k'-1}(1-\phi)^{k-1}}{[(1-\phi)k + \phi k']^{k+k'+1}} \quad (18)$$

and to use different values of k and k' . In order to try to be clear, we have assumed that the polydispersity of the first sequence (a) is $n_w/n_n = 1.1$; it is rather monodisperse, and we vary the polydispersity of the other sequence over the whole available spectrum. More precisely, going from the top curve to the bottom curve, the polydispersity of b takes the values 1.01–1.1–1.5–2–11. From these curves, one can draw the following conclusions. The position of the maximum (when it does exist) shifts with the polydispersity. Experimentally, this could be an indication about the dissymmetry of the polydispersity. If both sequences have the same polydispersity, the maxi-

imum stays at $\phi = 0.5$; if not, the maximum shifts toward the higher volume fraction of the most polydisperse sample. (There is no simple explanation of this fact.) This result could offer perhaps a possibility when one knows the polydispersity of one part of the copolymer to determine the polydispersity of the other by measuring the exact position of the maximum. For $k = 2$, the curve is very peculiar; at $\phi = 0$, it reaches a constant value; at $\phi = 1$, it goes to zero. This is reminiscent of the behavior for $k = k' = 1$ and $\phi = 0.5$, where the diagram is a horizontal line. Since k has been chosen larger than one, there is a range of values of k' (smaller than one) or $\bar{n}_{wb}/\bar{n}_{bn} > 2$ where the curve (see curve 5 on Fig. 4) is asymmetrical: it begins with a maximum at high ϕ , followed by a deep minimum and by a new increase when ϕ reaches zero. All these results, which, in a certain way, are astonishing, need to be confirmed by experiments.

The Two Sequences of the Copolymer Have Different Lengths and the Same Polydispersity

We have to go back to eq. (17), writing this time, $k = k'$. Keeping an arbitrary value for ϕ_0 leads to

$$\gamma(\phi) = \frac{\Gamma(2k)}{[\Gamma(k)]^2} 2\phi_0^{k+1}(1-\phi_0)^{k+1} \times \frac{[\phi(1-\phi)]_{k-1}}{[\phi - 2\phi\phi_0 + \phi_0]_{2k+1}} \quad (19)$$

In Figure 5, we have plotted $\gamma(\phi)$ as a function of ϕ for block copolymers with the same polydispersity ($n_w/n_n = 1.1$) but different compositions. When the composition tends either to one (or zero), the peak become sharper. This result could have been expected since, when one reaches the limit $\phi_0 = 0$ or 1, the system becomes monodisperse in composition, regardless of the polydispersity of the sequences.

The General Case

Equation (17) allows us to make graphs for all values of the three parameters defining the systems: the ratio of the number-average to the weight-average DP and of the a and b parts, and the composition of the copolymer. This will be interesting only when experimental results will be available, and one could compare them with theory. The only result we would like to show corresponds to the comparison of two systems for which $\phi_a = 0.1$. One sees that these two copolymers of the same composition have very different chromatograms when their polydispersities, which are not very different ($n_w/n_n = 1.1$ and 1.25), are exchanged between part a and part b. This means that this type of chromatography is very sensitive to the composition of copolymers and should be an excellent tool for their characterization (see Fig. 6).

If one goes back to Figure 1, one sees that the broadening of the peak by polydispersity is important, since going from $n_w/n_n = 1$ to 2. For each se-

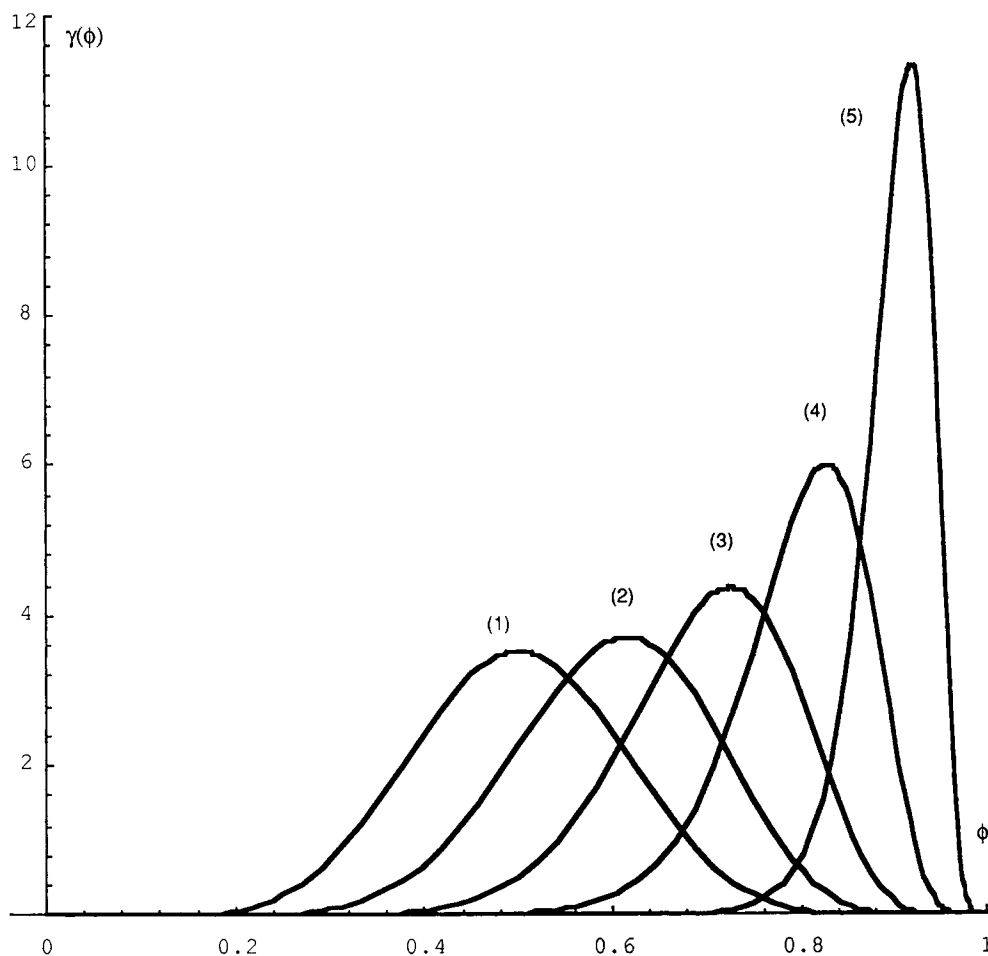


Figure 5 The function $g(\phi)$ for $n_{wa}/n_{na} = n_{wb}/n_n$ and different values of ϕ_0 : (1) $\phi_0 = 0.5$; (2) $\phi_0 = 0.6$; (3) $\phi_0 = 0.7$; (4) $\phi_0 = 0.8$; (5) $\phi_0 = 0.9$.

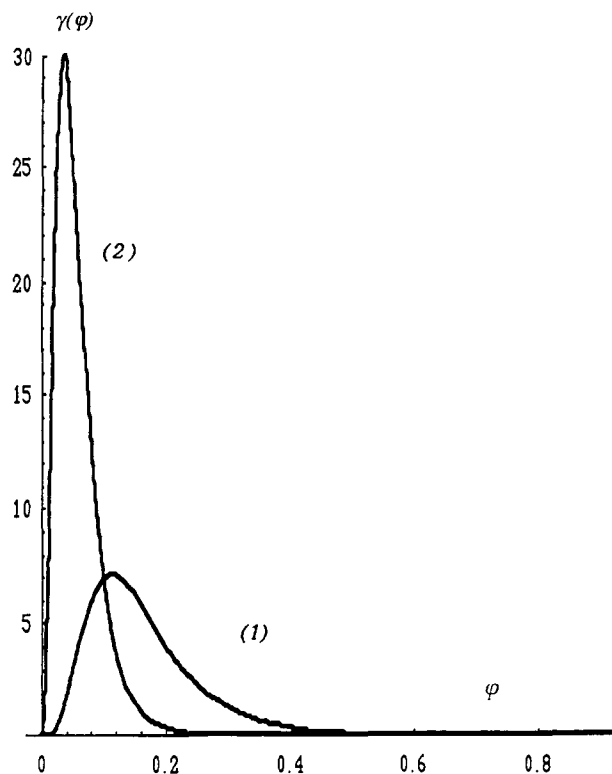


Figure 6 Chromatograms corresponding to two different copolymers. Case (1): $n_{wa}/n_{na} = 1.115$; $n_{wb}/n_{nb} = 1.22$; $\phi_a = 0.1$. Case (2): $n_{wa}/n_{na} = 1.22$; $n_{wb}/n_{nb} = 1.15$; $\phi_a = 0.1$.

quence, one goes from a delta function to the absence of a peak; this leads to the conclusion that axial dispersion and all the effects that contribute to the natural width of a chromatographic peak should be less disturbing in this type of chromatography than in the classical size exclusion chromatography.

This leads to the following conclusions.

- 1) Adsorption chromatography seems to be an excellent tool for studying copolymers. Some work has already been done in this domain,^{2,3} but this technique should be more often utilized by people interested in the structure of copolymers.
- 2) The results that have been presented here seem to show that the effect of axial broadening, regardless of its origin, is much less important in this type of chromatography than in the size exclusion chromatography if one succeeds to satisfy the hypothesis made at the beginning of this paper, i.e., the absence of effect of molar mass and structure on the elution composition.

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