

Analysis of block copolymers by high-performance liquid chromatography under critical conditions

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ABSTRACT

The complete chromatographic characterization of block copolymers (molecular weight *versus* chemical composition) is an important problem in polymer chemistry. The experimental validity of the concept of so-called “chromatographic invisibility”, predicted theoretically by Gorbunov and Skvortsov on the basis of the phenomenon of critical conditions known in liquid chromatography, was examined. The theoretical approach predicts the possibility of one component of an A–B block copolymer being eluted under gel permeation chromatographic conditions, whereas the size of the alternate “invisible” component exerts no effect on the overall elution profile of the block copolymer. This applies only when special thermodynamic conditions, *i.e.*, eluent composition and temperature, are fulfilled, where the distribution coefficient *K* is unity, regardless of molecular weight. Block copolymers of poly(styrene–methyl methacrylate) and poly(styrene–*tert.*-butyl methacrylate) were used as examples with binary and ternary mixtures of acetonitrile–dichloromethane, methanol–chloroform, tetrahydrofuran–dichloromethane and tetrahydrofuran–dichloromethane–hexane as eluents for chromatography under critical conditions on wide-pore silica gel in narrow-bore columns.

INTRODUCTION

Compositional and molecular weight distributions in block copolymers are strongly correlated with the mechanical and hydrodynamic properties of these macromolecular compounds. The evaluation of these data is an important problem in polymer chemistry, for which chromatographic methods can be used. The most advantageous chromatographic approach available at present is so-called orthogonal chromatography [1–3], or the combination of separations in different dimensions,

i.e., size and composition. An example is the combination of gel permeation chromatography (GPC) and gradient (normal- or reversed-phase) chromatography, where the gradient step is used for evaluating the compositional distribution.

However, the application of isocratic chromatography in evaluating compositional heterogeneity data may be more advantageous than the gradient mode, primarily owing to the better reproducibility of retention time data in equilibrated systems without the recovery stage. Another problem in gradient separations is the variation of the background absorption in the ultraviolet region, commonly used for detection, of the eluents most frequently used in polymer analysis [1]. The “invisibilities” concept [4] is useful in that it allows the molecular weight of the

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structural units in block copolymers to be evaluated directly, which is not possible with other chromatographic methods.

Taking these considerations into account, the approach developed theoretically [4] and presented here as an experimental methodology seems to have inherent advantages. The method enables steric exclusion effects in chromatography to be suppressed for some defined parts of a copolymer, so that they become invisible, thus enabling another, visible part of the molecule to be evaluated under GPC conditions, as if it were being chromatographed separately. This approach is based on a theoretical treatment described elsewhere [4,5]. Some earlier experimental results assessing the validity of the concept of invisibility have been presented previously [6].

The objectives of this present study were to explore this concept under a variety of chromatographic conditions and to examine the influence of different factors (such as mobile phase composition, temperature and molecular weight of the sample) on the chromatographic zone profile of poly(methyl methacrylate) (PMMA) and poly(*tert.*-butyl methacrylate) (PtBMA). It was hoped to evaluate the mechanism of adsorption over the range of conditions examined.

THEORETICAL BACKGROUND

Critical conditions in the liquid chromatography of polymers represent the thermodynamic state where the distribution coefficient of a polymer becomes unity ($K = 1$), regardless of its molecular weight. This phenomenon has been examined by some workers [7–9] in the context of the concept of a universal mechanism in chromatography and it was shown that the most important parameter that defines the chromatographic behaviour of a polymer is the energy, $-\varepsilon$, of interaction of a polymer segment and the sorbent. This parameter depends on the thermodynamic state of the system and assumes a specific value when the chromatographic state of the system undergoes a transfer from exclusion to adsorption conditions. The data obtained were interpreted as a phase transfer, and exclusion–adsorption was considered as a manifestation of the universal law of chromatography. The range of thermodynamic conditions over which this

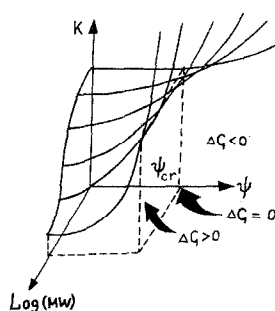


Fig. 1. Distribution coefficient, K , versus logarithm of molecular weight, $\log(MW)$, and volume fraction of eluent modifier, ψ . $\Delta G = -kT \ln K$, where k is Boltzmann's constant and T is absolute temperature.

phase transfer occurred were defined as the critical conditions, for which the appropriate energy was $-\varepsilon_{cr}$. Thus the range corresponding to GPC can be defined as that where $-\varepsilon < -\varepsilon_{cr}$ ($\Delta G > 0$), while the range of adsorption corresponds to $-\varepsilon > -\varepsilon_{cr}$ ($\Delta G < 0$), as illustrated in Fig. 1. Under critical conditions, where ($\Delta G = 0$) a homopolymer elutes with the total volume of the column, regardless of its molecular weight. ΔG is the change in conformational free energy of the macromolecule when it enters the pore.

This phenomenon has been confirmed experimentally for different types of polymers and sorbents [7,9]. A theoretical approach has been developed by Gorbunov and Skvortsov [4,5] on the basis of Cassasa's theory of the chromatography of macromolecules [10]. They proposed the term "chromatographic invisibility" to describe the insensitivity of a chromatographic system to the molecular weight of a polymer under these particular conditions. They applied the idea of chromatographic invisibility in developing a theory for the separation of block copolymers of the A–B type, according to the lengths of the "visible" blocks only, in some types of copolymers with complicated architecture in pores of arbitrary diameter. They have also shown that the theory is valid in general for cases when the invisible blocks possess a free terminus on the chains. This approach was developed theoretically for flexible-chain macromolecules, assuming no excluded volume effects in slit-like pores.

The main statements of the theory developed by Gorbunov and Skvortsov [4] are as follows. According to the basic approach of Cassasa [10] under the

above conditions, the distribution coefficient of the macromolecule, K , is equal to the ratio of the free energies of a macromolecule in and out of the pore, which in general can be written as

$$K = D^{-1} \int_0^D Z(x) dx \quad (1)$$

where $Z(x)$ is the statistical sum of the chain, one end of which is at a distance x from the pore wall, and D is the width of the slit-like pore.

On this basis, and after introducing the appropriate value of the energy of interaction of the chain segment with the pore wall, it was shown that under critical conditions the statistical sum of the chain is $Z_{cr}(x) = 1$, for any size of macromolecule and D and for all x , and consequently $K_{cr} = 1$. On the same basis, for a block copolymer of the A-B type, the expression for K can be defined as

$$K_{AB} = D^{-1} \int_0^D Z_A(x) Z_B(x) dx \quad (2)$$

where $Z_A(x)$ and $Z_B(x)$ are the statistical sums of the appropriate blocks. Hence, if critical conditions are established for block B, then $Z_B(x) = 1$, so that K_{ABcr} of the total block copolymer molecule is given by the following expression:

$$K_{ABcr} = D^{-1} \int_0^D Z_A(x) dx = K_A \quad (3)$$

which means that block B becomes chromatographically invisible.

It was of interest to check the validity of this concept experimentally with real block copolymers. For this purpose, the simplest block copolymers of the A-B type were chosen. Eqn. 3 as developed by Gorbunov and Skvortsov [4] was taken as the basic concept of this work in developing a method to determine the polydispersity and compositional heterogeneity in block copolymers.

EXPERIMENTAL

Equipment

Standard chromatographic equipment used in-

cluded a Model 3000 spectrophotometer (LDC Analytical, Riviera Beach, FL, USA) with cell volume $1.5 \mu\text{l}$, two LKB model 2150 pumps (Pharmacia, Uppsala, Sweden) with a PU404 solvent mixer (Philips Analytical, Cambridge, UK) for regulation of the binary mixed mobile phase composition, a Rheodyne (Cotati, CA, USA) Model 7125 injection valve with a $1\text{-}\mu\text{l}$ loop and a TC 931 column heater (Applied Chromatography Systems, Macclesfield, UK).

Columns

Normal-phase S5X silica gel of $5\text{-}\mu\text{m}$ particle size and $300\text{-}\text{\AA}$ pore diameter (Phase Separations, Clwyd, UK) was packed in a stainless-steel column ($250 \text{ mm} \times 2 \text{ mm I.D.}$). The column was calibrated with polystyrene (PS) and PMMA standards over the molecular weight range $1700\text{--}1\,950\,000$ obtained from Polymer Labs. (Church Stretton, UK). The column efficiency for benzene was $28\,000$ theoretical plates/m.

Another type of silica gel, LiChrospher Si-300, also of $5\text{-}\mu\text{m}$ particle size and $300\text{-}\text{\AA}$ pore diameter (Merck, Darmstadt, Germany), was packed in a fluoroplastic column ($350 \text{ mm} \times 0.5 \text{ mm I.D.}$) [6]. The calibration procedure was the same as that for the S5X silica gel and the column efficiency for benzene was $29\,000$ theoretical plates/m.

Calculation procedures

The peak asymmetry was calculated according to the standard procedure. A perpendicular was drawn from the peak maximum to the baseline. At a point 10% from the baseline the segments to the leading and tailing edges (A and B, respectively) were measured. The asymmetry was obtained by dividing of length of the tailing segment, B, by that for the leading segment, A.

The equilibrium distribution of the split zones, defined here as the apparent distribution coefficient, $\langle K \rangle$, was measured as the ratio of the peak areas of the two zones observed for PtBMA under near-critical conditions. The range of the $\langle K \rangle$ value was the same as that for the conventional distribution coefficient, K .

Eluents

The eluent components used were dichloromethane (DCM), chloroform (CHL), acetonitrile (ACN),

TABLE I
CHARACTERISTICS OF BLOCK COPOLYMERS

Sample	Molecular weight	PS weight fraction (%)
P(S-tBMA)		
No. 53	70 000	19.0
No. 41	95 000	5.0
No. 11	100 000	2.5
No. 31	130 000	50.0
P(S-MMA) ^a		
No. 1	14 000	50.0
No. 2	35 000	50.0
No. 3	58 000	50.0
No. 4	107 800	50.0

^a Manufacturer's data based on NMR.

methanol (MET), tetrahydrofuran (THF) and *n*-hexane (HEX), all of high-performance liquid chromatographic grade. Mixed mobile phases were made by volume mixing and then their compositions were regulated precisely by the two pumps.

Samples

A-B-type block copolymers of poly(styrene-*tert*-butyl methacrylate) P(S-tBMA) were obtained by successive anionic polymerization at the Institute of Macromolecular Compounds Academy of Sciences (St. Petersburg, Russia) according to the procedure described previously [11,12], which permits the preparation of linear narrow-disperse polymers. PS precursors were collected directly from the reactor after the first stage of the process; hence it was possible to obtain the molecular weight characteristics of the PS blocks of the block copolymers.

Block copolymers of poly(styrene-methyl methacrylate) P(S-MMA) were obtained from Polymer Labs. The molecular characteristics of the samples are described in Table I. All the samples of homopolymers and block copolymers were dissolved in the mobile phase at a concentration of *ca.* 0.1% (w/v) and aliquots of 1 μ l were injected.

Samples of isobutyl methyl ketone, methyl ethyl ketone and acetone were all of analytical-reagent grade and were injected into the column without dilution.

RESULTS AND DISCUSSION

Chromatography of polymers under critical conditions

The eluent required to give critical conditions for polar blocks (PMMA, PtBMA) of block copolymers on silica gel sorbent was found by varying the percentage of the polar component. For non-polar blocks (PS), GPC conditions were expected. However, it is necessary to bear in mind the dependence of the thermodynamic properties of an eluent, as determined by its composition and temperature, in order to avoid a shift of the retention time of PS as a result of changes in the Mark-Kuhn constants, *i.e.*, owing to a change in the size of the macromolecule. These conditions were established using the eluent system DCM-ACN with restricted amount of ACN owing to the problems of solute solubility. DCM is a good solvent for all the samples, whereas for PS it creates size-exclusion conditions in chromatography. On the other hand, PMMA and PtBMA are totally adsorbed. ACN as a desorption component

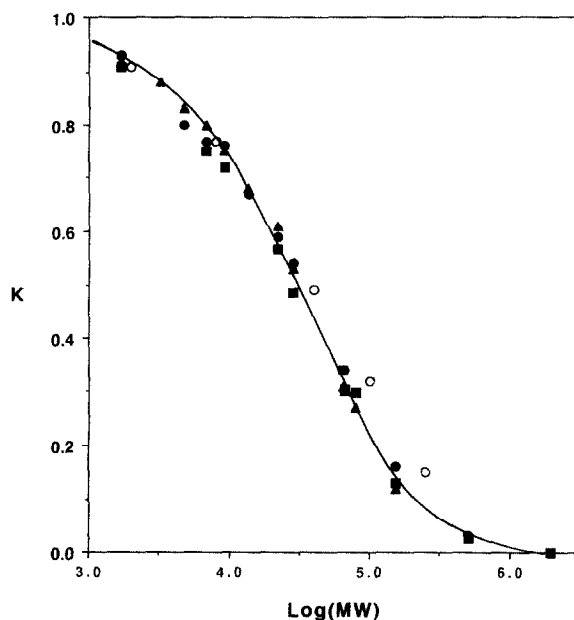


Fig. 2. Calibration graphs of distribution coefficient, K , versus logarithm of molecular weight, $\log(MW)$, for PS standards in different eluents: (▲) THF; (●) ACN-CHL (47:53, v/v); (■) MET-CHL (20:80, v/v); and (○) ACN-DCM (1:1, v/v). Column: 350 \times 2 mm I.D., packed with silica gel S5X (this column was used in all the experiments except as noted in the text).

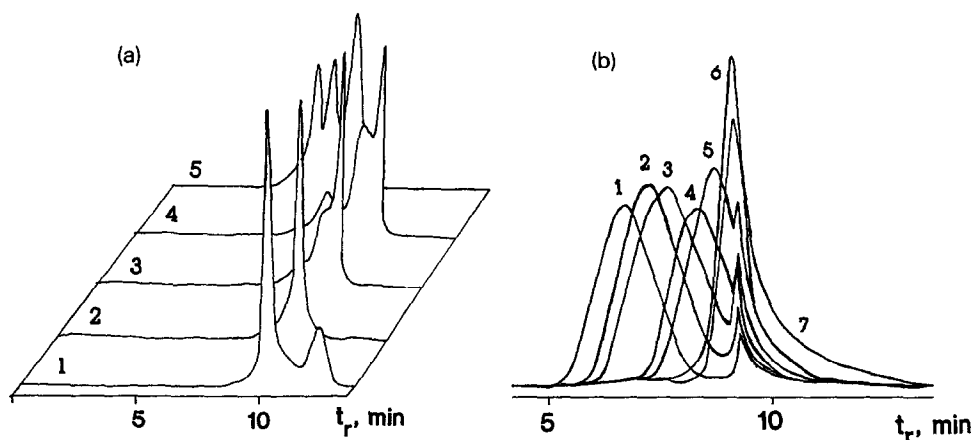


Fig. 3. Chromatographic zone shift under near-critical conditions. Column: 350×0.5 mm I.D., packed with LiChrospher Si-300. (A) PMMA (MW 27 700, 60 000, 107 000). Eluent, ACN-DCM: (1) 42.8:57.2; (2) 43.0:57.0; (3) 43.1:56.9; (4) 43.3:56.7; (5) 46.0:54.0 (v/v). (5) GPC, (2) critical and (1, 3 and 4) near-critical conditions. (B) PtBMA (MW 80 000). Eluent, ACN-DCM: (1) 11.2:88.8; (2) 10.6:89.4; (3) 10.3:89.7; (4) 9.9:90.1; (5) 9.6:90.4; (6) 9.3:90.7; (7) 9.0:91.0 (v/v). (1) GPC, (6) critical and (2, 3, 4, 5 and 7) near-critical conditions.

of the eluent is appropriate for PtBMA because small amounts (less than 10%) are sufficient, with no problem with solubility. However, ACN is less successful for PMMA, because considerable concentrations of ACN are necessary for its desorption, and these are near the limits of solute solubility. As a result, a slight shift of the calibration dependence was observed for PS under the critical conditions for PMMA. However, this shift was considered to be negligible, because it did not exceed a value of 5% in different eluents over the range of molecular weights of interest (Fig. 2). On the basis of these data, it may be assumed that PS elutes by a GPC mechanism.

Another desorptive component used in the binary mixed mobile phase with DCM was THF, which did not lead to any problems with solubility, but did influence the shape of the calibration dependence under critical conditions. However, this shift was not substantial and was not taken into account (Fig. 2).

As has been shown previously for other polymers [7-9], critical conditions exist for a particular eluent composition and sorbent. In this work they have been found for PMMA and for PtBMA in eluent systems containing two or three components of different polarity. These systems were ACN-DCM, ACN-CHL, MET-CHL, THF-DCM and THF-HEX-DCM. In the range of molecular weights from 20 000 to 100 000, a shift of peak position and a change in elution order, as described earlier for other

polymers, was observed under adsorption conditions (Fig. 3).

For higher molecular weight samples, a splitting of zones and reversible pumping of samples from the GPC zone to critical conditions was observed for both PMMA and PtBMA. The results for PMMA standards in the system MET-CHL, shown in Fig. 4, indicate the strong dependence of peak shape on the molecular weight of PMMA, which manifested itself in splitting of the chromatographic zone followed by considerable peak tailing. For the PtBMA sample in the THF-DCM system, peak splitting indicates another mechanism of sorption with division of the zone into two zones, one of which elutes under GPC conditions and another under critical conditions, where the fraction of the zones changes in accordance with the thermodynamic state of the chromatographic system. However, both zones have a regular shape without any tailing.

The data on the influence of temperature on the distribution coefficients of the PMMA standards in the binary eluent system ACN-CHL (1:1, v/v) are shown in Fig. 5. The relationships have a regular character and the distribution coefficients gradually shift to unity when the temperature increases. These data are in qualitative agreement with those obtained for PS in the system CHL-tetrachloromethane [7].

An investigation of the relationship between

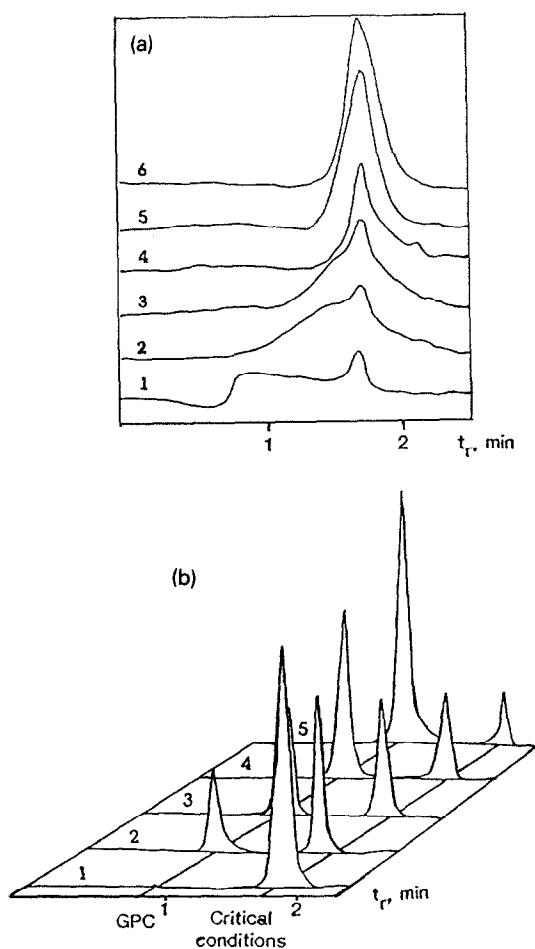


Fig. 4. Influence of molecular weight of the samples on (A) chromatographic zone profiles under near-critical conditions for PMMA (A) and (B) zone splitting for high-molecular-weight PtBMA. (A) PMMA MW: (1) 400 000; (2) 265 000; (3) 185 000; (4) 107 000; (5) 82 000; (6) 60 000. Eluent: MET-CHL (20:80, v/v). (B) PtBMA MW: 200 000. Eluent, THF-DCM: (1) 5.0:95.0; (2) 5.4:94.6; (3) 5.85:94.15; (4) 6.5:93.5; (5) 9.0:91.0 (v/v).

the thermodynamic state of the chromatographic system, *i.e.*, mobile phase composition, and the retention characteristics in the range of near-critical conditions was performed on the basis of approaches developed by Scott and Kucera [13,14] by comparing the behaviours of related substances with polarity values close to those of PMMA and PtBMA. The relationships between the reciprocal of the corrected retention volume, $1/V_R$, and the volume fraction of solvent modifier were obtained for

isobutyl methyl ketone, methyl ethyl ketone and acetone (Fig. 6). The retention behaviour of each of these substances was then compared with those of PMMA and PtBMA. For both eluent systems, ACN-DCM and THF-DCM, the relationships show a non-linear character over a wide range of eluent composition. This behaviour was of the type observed previously by McCann *et al.* [15] and designated a "type VI" system. These relationships can be approximated by two linear regions with different slopes. According to data obtained by Scott and Kucera [14], these areas could possibly be interpreted as the areas of monolayer formation and slow double-layer formation, respectively. Comparison of these relationships with the graphs of the distribution coefficient of PMMA, K , and the apparent distribution coefficient for PtBMA, $\langle K \rangle$, shows that critical conditions may exist in the range of mobile phase composition of THF-DCM, corresponding to the completion of monolayer formation (Fig. 6) and where retention has a displacement character. All the values are plotted on the same numerical scale. Analogous relationships were obtained for the eluent ACN-DCM.

These data are in agreement with those obtained

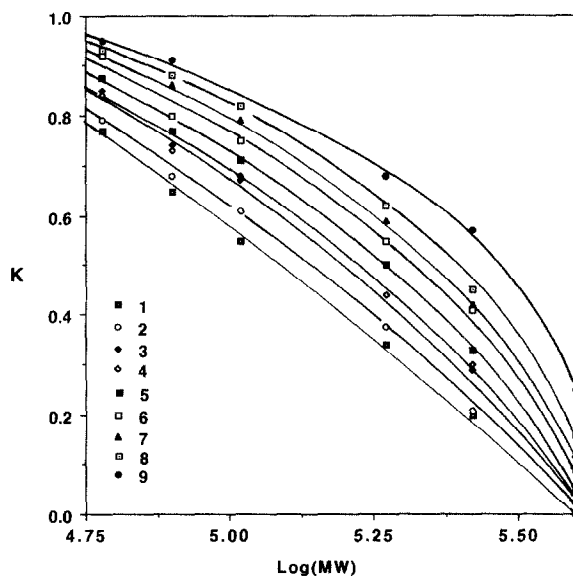


Fig. 5. Relationships between the distribution coefficients and $\log(\text{MW})$ for PMMA standards at different temperatures. Eluent: CHL-ACN (1:1, v/v). (1) 25; (2) 30; (3) 35; (4) 37; (5) 40; (6) 42; (7) 45; (8) 47.2; (9) 50.2°C.

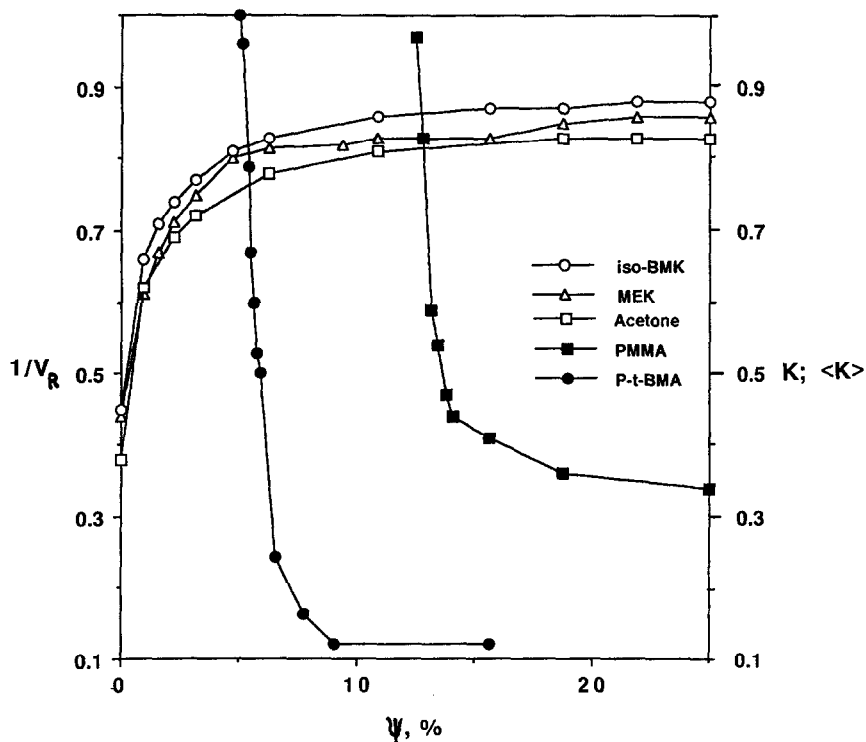


Fig. 6. Comparison of the relationships between the reciprocal of retention volume, $1/V_R$, for (○) isobutyl methyl ketone, (△) methyl ethyl ketone and (□) acetone and the volume fraction of THF in the eluent (THF-DCM), and that of the distribution coefficient, K , for (■) PMMA (MW 82 000) and the apparent distribution coefficient, $\langle K \rangle$, for (●) PtBMA (MW 200 000) (see text) under the same conditions.

by Tennikov *et al.* [7] for PS in the system tetrachloromethane-chloroform. The nature of the monolayer formed on the surface of silica gel apparently plays an important role in the mechanism of retention of polymers under near-critical conditions. The addition of a non-polar component, *n*-hexane, which may, according to Scott and Kucera's data [13,14], lead to dense bilayer formation, changes the shapes of the chromatographic zones considerably. In Fig. 7, the relationship between the asymmetry of the chromatographic zone profiles for PtBMA and the volume fraction of the eluent modifier is shown for the systems HEX-THF and HEX-DCM-THF. In the former system, where bilayer formation can be expected, considerable asymmetry and peak tailing were observed, whereas addition of DCM led to a considerable decrease in asymmetry. These data show the significance of the nature of the polar component layer as regards the chromatographic behaviour of polymers

under near-critical conditions, an observation which needs further systematic investigation.

Chromatography of block copolymers under critical conditions

The next step was to examine the validity of the theoretical concept of chromatographic invisibility for evaluating the molecular characteristics of block copolymers.

When critical conditions apply for one of the blocks of a block copolymer of the A-B type, so that according to theory [4] it becomes chromatographically invisible, it can be expected that the chromatogram of the block copolymer will coincide with that for the visible block (PS block), at least so far as the positions of their peaks are concerned. Prediction is limited to peak positions, as the theoretical basis for this effect is developed only in terms of equilibrium distribution coefficients, and does not take into account the dynamics and kinetics of the

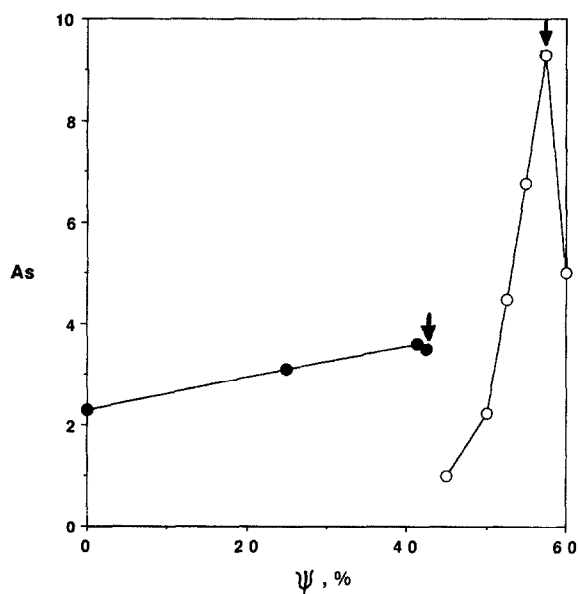


Fig. 7. Relationships between asymmetry, A_s , and volume fraction of eluent modifier, ψ , for PtBMA (MW 200 000) in different eluents: (○) HEX-THF and (●) HEX-THF-DCM (THF-DCM constant at 1:1, v/v; variable HEX, ψ). Arrows indicate the critical conditions for PtBMA.

processes that are responsible for the shape of the peak profiles. The experimental results obtained confirm this prediction.

Hence the values of retention times, t_r , in the chromatograms of P(S-tBMA) samples (Table I) and their PS precursors coincide in the eluent system ACN-DCM (9.3:90.7, v/v; 25°C) (Fig. 8). In the

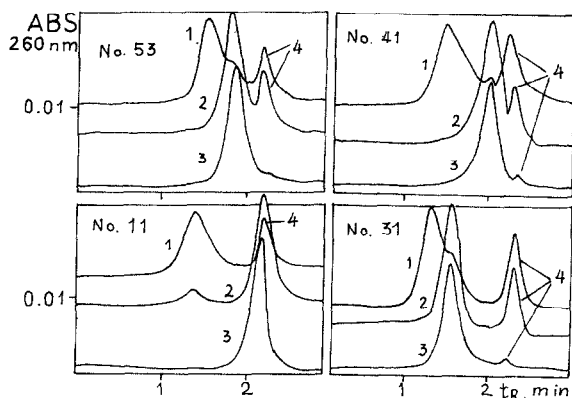


Fig. 8. Chromatograms of P(S-tBMA) and PS precursors with ACN-DCM as eluent. (1) GPC; (2) critical conditions; (3) PS precursor; (4) impurity.

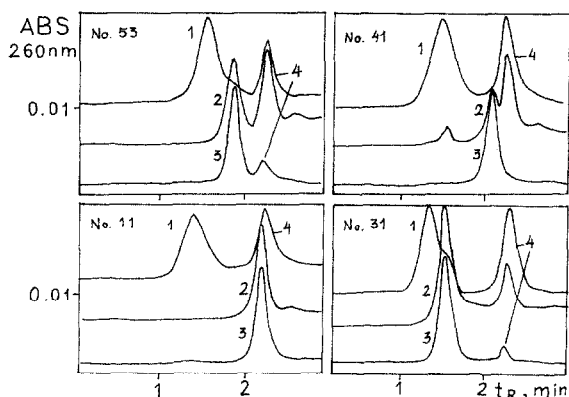


Fig. 9. As Fig. 8 with THF-DCM as eluent.

system THF-DCM, good coincidence of the chromatograms of PS and of the related block copolymers under critical conditions (5.5:94.5, v/v; 28°C) was clearly achieved (Fig. 9).

It should be noted that the absolute value of the eluent composition can vary in the range 5–10%, depending on the water content of the solvent and on the state of the silica gel. It is likely that the validity of this concept is limited to visible blocks whose size exceeds a certain minimum, as implicated in Table I.

APPLICATIONS

The methodology described above was applied to the analysis of block copolymers of P(S-MMA) (Table I). The data presented in Table II show the

TABLE II
PS WEIGHT FRACTIONS IN BLOCK COPOLYMERS OF P(S-MMA) EVALUATED BY MEANS OF CHROMATOGRAPHY UNDER CRITICAL CONDITIONS

Molecular weight of block copolymer	Apparent molecular weight of block copolymer under critical conditions ^a	Weight fraction of PS (%)
107 800	49 000	46
58 500	24 000	42
35 000	15 000	43
14 000	7000	50

^a Apparent molecular weight was evaluated with the help of a calibration graph with respect to PS standards.

values of the PS fraction in block copolymers obtained by means of chromatography under critical conditions, where block copolymers are eluted as pure PS blocks in GPC. The data can be considered as reasonable and accepted as one of the first examples showing the additional possibility of evaluating of block copolymer heterogeneity.

CONCLUSIONS

The theoretical prediction of the chromatographic invisibility of individual blocks in block copolymers under critical conditions has been confirmed experimentally for the case of A-B block copolymers of P(S-MMA) and P(S-tBMA) with molecular weights up to 100 000 in wide-pore silica gel. Under these conditions, block copolymer macromolecules elute according to the size of the visible block.

It was found that critical thermodynamic conditions are feasible when the monolayer formation on the silica gel surface is complete. The shape of the zone profile under near-critical conditions is influenced by the molecular weight of the polymer (*i.e.*, by the ratio of the size of the molecule to that of the pore) and by the nature of the polar component layer on the surface of the silica gel.

The data obtained suggest possibilities for the direct, non-destructive analysis of individual components of complex macromolecules.

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