

Chromatographic investigations of macromolecules in the critical range of liquid chromatography: 4. Analysis of poly(styrene-*b*-methyl methacrylate)

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Poly(styrene-*b*-methyl methacrylate)s were analysed by liquid chromatography at the critical point of adsorption. By operating at chromatographic conditions corresponding to the critical mode for poly(methyl methacrylate) and the size exclusion mode for polystyrene, the molar mass and the polydispersity of the polystyrene block in the block copolymers may be determined. The data were found to be in excellent agreement with the corresponding parameters of the polystyrene precursor homopolymers.

(Keywords: liquid chromatography; critical point of adsorption; poly(styrene-*b*-methyl methacrylate); analysis)

INTRODUCTION

Block copolymers are complex macromolecular systems that are characterized by distributions in molar mass (*MMD*) and chemical composition (*CCD*). The determination of the *MMD* and *CCD* is possible using chromatographic cross-fractionation, where two different chromatographic techniques are combined. One of these (usually s.e.c.) provides information on the *MMD* whereas the other (gradient elution or precipitation chromatography) is sensitive towards the *CCD*¹.

Another more recent approach is the concept of 'invisibility', which assumes that chromatographic conditions exist under which heteropolymers can be separated according to the size of one of the components only, because the second component is chromatographically 'invisible'^{2,3}. The 'invisibility' concept experimentally relates to liquid chromatography at the critical point of adsorption, which was developed by Entelis *et al.* as a method for the determination of the functionality-type distribution (*FTD*) of telechelic oligomers and polymers⁴⁻⁶.

In brief, for every chromatographic process, the distribution of a solute between the stationary and mobile phases is related to the change in free energy ΔG . ΔG depends on the solute/macromolecule size, the pore size of the stationary phase and the energy of interaction, $\epsilon(x)$, of the monomer unit and the segment of the stationary phase surface. Starting with a critical potential of interaction, ϵ_c , adsorption of the macromolecule takes place in the pore ($\epsilon > \epsilon_c$).

At $\epsilon < \epsilon_c$ the macromolecule remains unadsorbed and at $\epsilon = \epsilon_c$ the interaction energy is exactly compensated

by the entropy losses. Corresponding to these three cases are the three modes of chromatography of macromolecules: adsorption, exclusion and critical. At the critical point ΔG is zero and $K_d = 1$ regardless of the molar mass. Accordingly, the chain length of the macromolecule does not contribute to retention, and retention depends only on the inhomogeneities of the polymer chain, i.e. the number and type of functional groups, grafting sites, blocks, etc.

It was shown by us^{7,8} and other authors^{9,10} that the 'invisibility' concept can be applied to the characterization of block copolymers. For example, taking a block copolymer $A_n B_m$, the block A_n may be regarded as a functional group or inhomogeneity. Therefore, using the critical conditions of B_m for the chromatographic separation, A_n may be analysed and vice versa.

The subject of the present paper is the analysis of block copolymers of styrene and methyl methacrylate. Operating at the critical point of poly(methyl methacrylate) (PMMA) the *MMD* of the polystyrene (PS) block will be determined and compared with the characteristics of the corresponding PS precursor homopolymers.

EXPERIMENTAL

Liquid chromatography at the critical point of adsorption was carried out on a modular h.p.l.c. system, comprising a Waters model 510 pump, a Waters differential RI detector R401, a Knauer u.v./vis. filter photometer, a Rheodyne six-port injection valve and a Waters column oven. The columns used were either a Macherey-Nagel Nucleosil Si-100, 5 μm average particle size, 200 \times 4 mm i.d., prepacked column or Merck LiChrospher Si-300 and

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Si-1000, 10 μm average particle size, 200 \times 4 mm i.d., self-packed columns.

The s.e.c. investigations were performed on a Waters modular s.e.c. system using six 300 \times 8 mm i.d. Waters Ultrastaygel columns (10^6 , 2×10^5 , 2×10^4 , 10^3 Å) and tetrahydrofuran (THF) as the mobile phase.

All solvents were Baker h.p.l.c. grade.

The poly(styrene-*b*-methyl methacrylate)s were prepared by anionic polymerization. Copolymers B1–B3 were prepared first by polymerizing styrene in THF at low temperature (-70°C) using phenylisopropylpotassium as initiator. In order to avoid the attack of the ester group of methyl methacrylate (MMA) by polystyryl carbanions, 1,1-diphenylethylene was introduced prior to the addition of MMA to decrease the nucleophilicity of the active sites. Samples B4 and B5 were prepared by butyllithium-initiated polymerization of styrene and subsequent addition of methyl methacrylate.

RESULTS AND DISCUSSION

Principally there are two ways to determine the *MMD* of one block component in a two-block copolymer A_nB_m :

(i) Using the critical conditions of block A for the chromatography, block B may be analysed. The distribution coefficient of the block copolymer in this case corresponds to the distribution coefficient of block B:

$$\varepsilon = (\varepsilon_A)_c \quad K_d^{AB} = K_d^B$$

(ii) At the critical conditions of block B, block A may be analysed, and K_d of the block copolymer corresponds to K_d of block A:

$$\varepsilon = (\varepsilon_B)_c \quad K_d^{AB} = K_d^A$$

Depending on the polarity of the blocks A and B, the block to be analysed may be eluted in a size exclusion or adsorption mode at the critical conditions of the other block. Thus, if the polarity of A is higher than that of B, then at the critical point of A the block copolymer is eluted in a size exclusion mode when silica gel is used as the stationary phase. In the case of a reversed-phase column, an adsorption mode would be operating. However, as in adsorption chromatography the distribution coefficient depends exponentially on the molar mass, irreversible adsorption could occur for high-molar-mass components. Therefore, in most cases it is useful to select chromatographic conditions corresponding to the size exclusion mode.

The poly(styrene-*b*-methyl methacrylate)s under investigation were prepared by phenylisopropylpotassium-(B1–B3) or butyllithium-(B4, B5) initiated polymerization of styrene and subsequent addition of methyl methacrylate. The polystyrene precursors (P1–P3) were isolated and characterized separately. It may be assumed that the polystyrene molar mass and polydispersity do not change during the formation of the diblock copolymer, and therefore these parameters must be equal for the precursor and the polystyrene block in the block copolymer. In order to prove the validity of the 'invisibility' concept for the determination of single blocks in diblock copolymers, the poly(styrene-*b*-methyl methacrylate)s are investigated at the critical conditions of poly(methyl methacrylate).

It was demonstrated in previous investigations that the critical point may be obtained by selecting a certain stationary phase and varying the mobile phase until the

molar-mass dependence of the retention time disappears. The behaviour of poly(methyl methacrylate)s of different molar masses on silica gel in mixtures of methyl ethyl ketone (MEK) and cyclohexane is shown in Figure 1.

At concentrations > 73 vol% MEK in the mixture, the retention time increases with decreasing molar mass and, therefore, the size exclusion mode is operating. Adsorption takes place at concentrations < 73 vol% MEK where the reverse molar mass vs. retention time behaviour is observed. The critical point of PMMA is obtained at a composition of 73 vol% MEK/27 vol% cyclohexane. At this point one retention time is obtained for all molar masses of PMMA. Accordingly, using these chromatographic conditions, block copolymers containing PMMA as one block component may be analysed with respect to the second block component.

Figure 2 shows the size exclusion chromatograms (s.e.c. 1, Ultrastaygel, THF) of three poly(styrene-*b*-methyl methacrylate)s and the corresponding polystyrene precursors. As was expected for anionic polymerization, the *MMD* is very narrow. The total molar mass of the block copolymers (calculated using a polystyrene calibration curve) is of the magnitude of about 180 000, whereas the polystyrene content varies between 30 and 70 wt% (see Table 1). In addition, two block copolymers with lower total molar masses (150 000 and 20 000) and a polystyrene content of about 50 wt% were investigated.

Compared to the molar-mass data given by the manufacturer, the obtained data on s.e.c. 1 are somewhat lower. However, s.e.c. data obtained on a second system (s.e.c. 2, silica gel, MEK) are in good agreement with s.e.c. 1. The reason for this mismatch is the quantification of the chromatograms. The manufacturer's data were obtained by s.e.c.-light scattering detection, whereas quantification of s.e.c. 1 and s.e.c. 2 was based on a polystyrene calibration curve and RI and u.v. detection.

The chromatograms of the block copolymer B3 at the critical point of PMMA together with those of the corresponding precursor P3 and a polystyrene calibration standard of comparable molar mass are given in Figure 3. As can be seen, all three chromatograms have similar shapes and retention ranges. In contrast to s.e.c.,

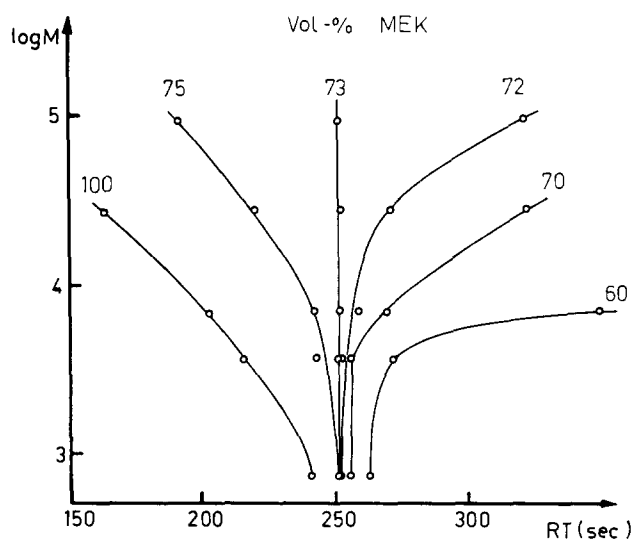


Figure 1 Critical diagram of $\log M$ vs. retention time of poly(methyl methacrylate); Nucleosil Si-100, MEK-cyclohexane, flow rate 0.5 ml min^{-1}

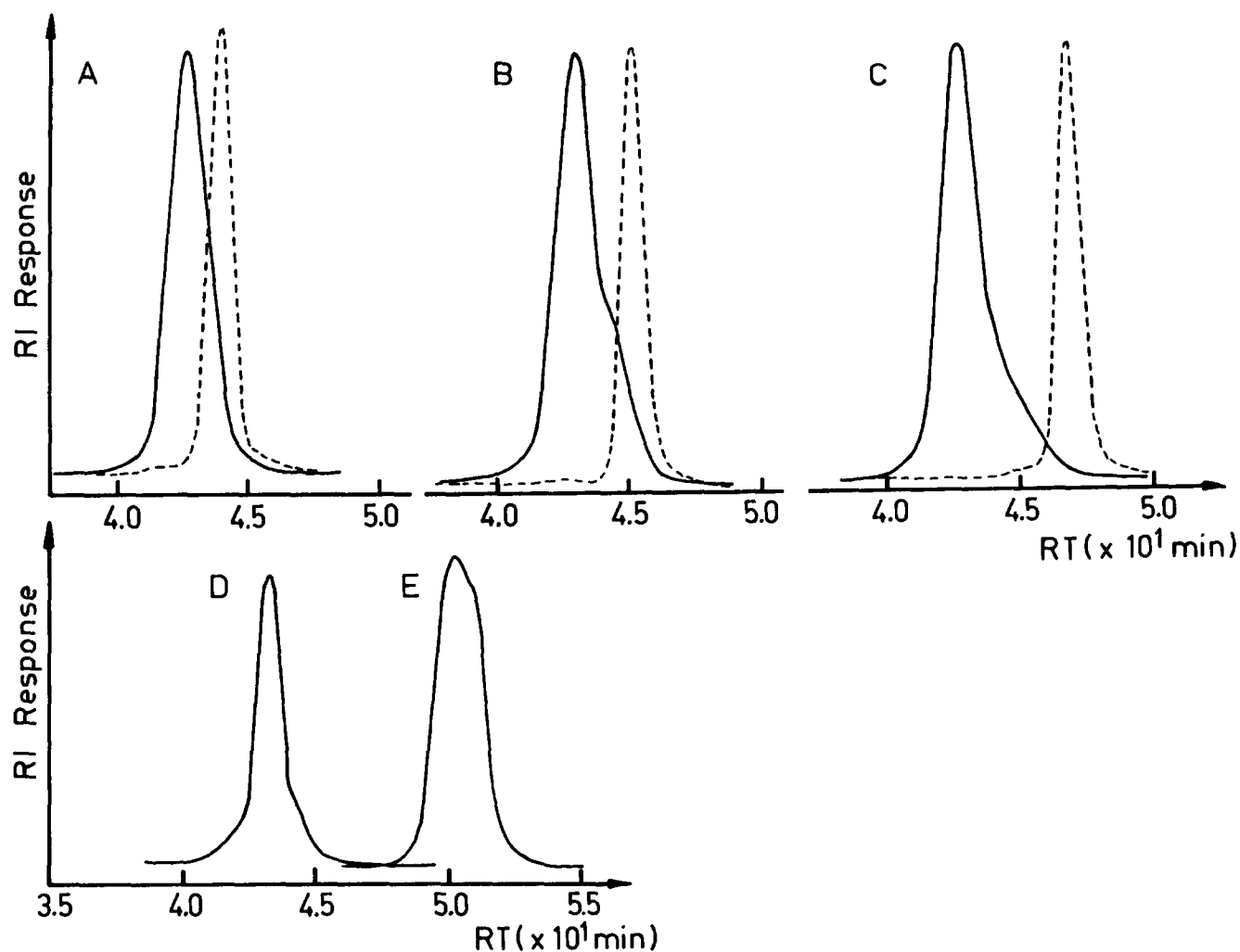


Figure 2 S.e.c. chromatograms of poly(styrene-*b*-methyl methacrylate)s (—) and their polystyrene precursors (---); Ultrastaygel 10⁶, 2 × 10⁵, 2 × 10⁴, 10³ Å, THF, flow rate 1 ml min⁻¹. (A) B1, P1; (B) B2, P2; (C) B3, P3; (D) B4; (E) B5

Table 1 Manufacturer's and s.e.c. molar-mass data of the samples

Sample	Manufacturer ^a <i>M_w</i>	S.e.c. 1 ^b		S.e.c. 2 ^c	
		<i>M_w</i>	<i>U</i>	<i>M_w</i>	<i>U</i>
P1	110 000	100 000	1.06	109 000	1.11
B1	165 000	152 000	1.08	153 000	1.15
P2	93 000	77 000	1.03	79 000	1.11
B2	182 000	141 000	1.15	156 000	1.16
P3	55 000	43 000	1.11	46 000	1.21
P3	188 000	140 000	1.11	134 000	1.21
B4	158 000	152 000	1.28		
B5	21 000	25 000	1.16		

^a S.e.c.-l.s.

^b S.e.c., polystyrene calibration, Ultrastaygel, THF

^c S.e.c., polystyrene calibration, LiChrospher Si-300 and Si-1000, MEK

Table 2 Molar-mass data from critical chromatography on a Nucleosil Si-100 stationary phase, with polystyrene calibration

Sample	<i>M_w</i>	<i>U</i>
PS 50 000	56 000	1.21
P3	42 000	1.38
B3	57 000	1.38
B4	67 000	2.34
B5	14 000	5.15

where the chromatograms of P3 and B3 are well separated, in the case of critical chromatography a nice overlay is obtained. This is a very strong indication for our assumption that at the critical point of PMMA the block copolymer behaves like the corresponding PS precursor homopolymer. Additional evidence is given by a tentative quantification of the chromatograms (see Table 2). The calculated molar masses and polydispersities are of the same magnitude; however, compared with the expected values (see Table 1) the polydispersities are too high. This is most obvious for the higher-molar-mass B4.

The chromatogram of the block copolymer B5 shows a bimodal distribution, which was not observed in the s.e.c. experiment. Probably, differences in polymer structure manifest themselves much more at the critical point. The type of this bimodality, however, may be determined only by preparative separation and analysing the two peaks.

The chromatograms of the highest-molar-mass samples P1, B1 and P2, B2 were of distorted shape and had an unusual broad distribution. This behaviour indicates that a part of the macromolecules does not fit into the pores of the stationary phase and separation takes place near the exclusion limit. Therefore, all further investigations were carried out on a two-column system comprising a LiChrospher Si-300 and a LiChrospher Si-1000 self-packed column.

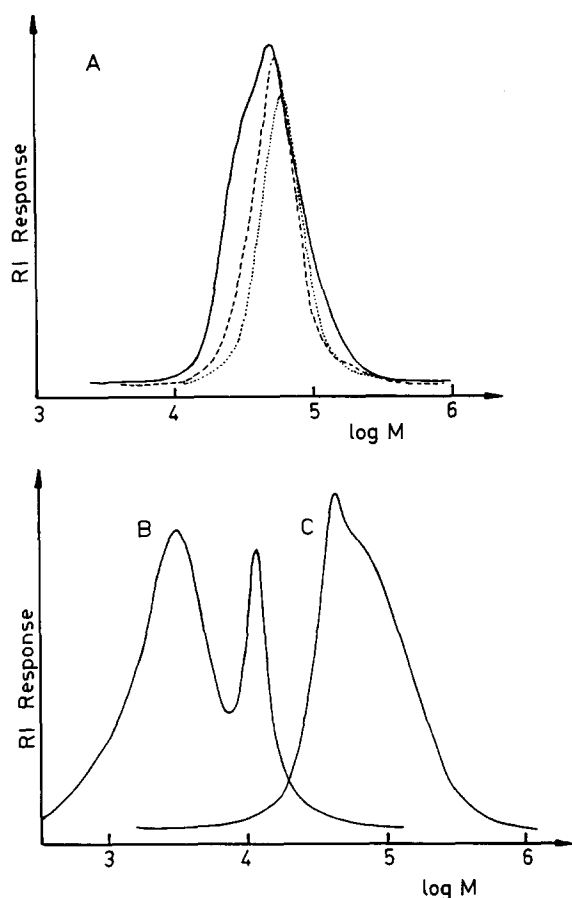


Figure 3 Chromatograms of the block copolymers (—), the polystyrene precursor P3 (---) and a PS calibration standard (···) at the critical point of PMMA; Nucleosil Si-100, MEK-cyclohexane 73:27 vol%. (A) B3; (B) B5; (C) B4

For this column system, which has slightly different silica gel surface characteristics, the mobile phase composition has to be adjusted accordingly. As can be seen in *Figure 4*, the critical point for PMMA is obtained at a mobile phase composition of 70 vol% MEK/30 vol% cyclohexane.

The h.p.l.c. analysis of a certain component in a complex mixture requires an appropriate separation as well as a sensitive detection. The separation is directed by the stationary and mobile phases of the chromatographic system, whereas the detection is determined by the sensitivity and selectivity of the detector. As for chromatography at the critical point of adsorption of block copolymers, it has to be assured that separation is accomplished with respect to only one block component. The same criterion must be observed for detection, i.e. for accurate quantification one block component must be selectively detected. The refractive-index detector, which is commonly used in s.e.c., is universal and therefore does not fulfil this criterion. For poly(styrene-*b*-methyl methacrylate)s the RI detector gives a response for the PS as well as the PMMA blocks. Accordingly, if the polydispersities of the two blocks differ significantly, quantification will give erroneous results. The most commonly used selective detector is the u.v./vis. photometer, where detection depends on the light absorption characteristics of the components. In our case a measuring wavelength of 280 nm was used, assuring

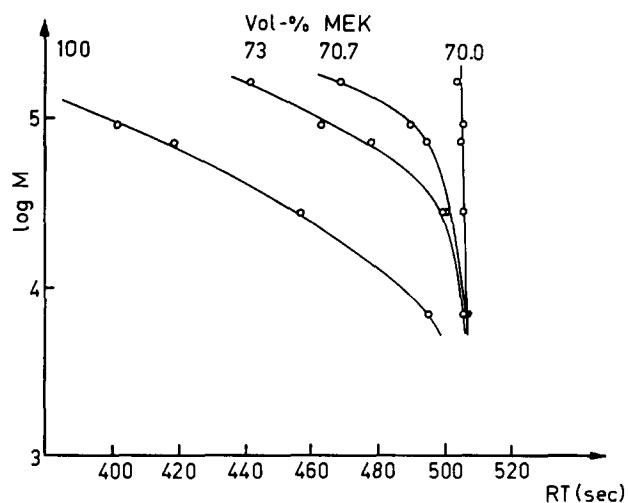


Figure 4 Critical diagram of $\log M$ vs. retention time of poly(methyl methacrylate); LiChrospher Si-300 and Si-1000, MEK-cyclohexane, flow rate 0.5 ml min^{-1}

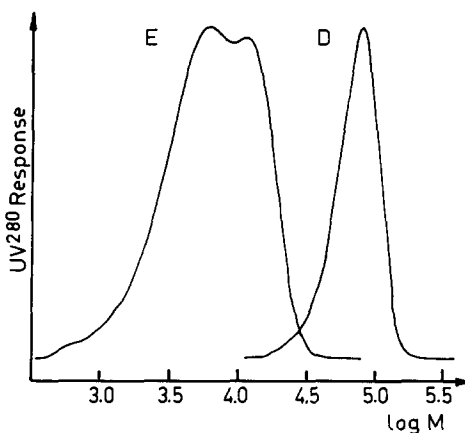
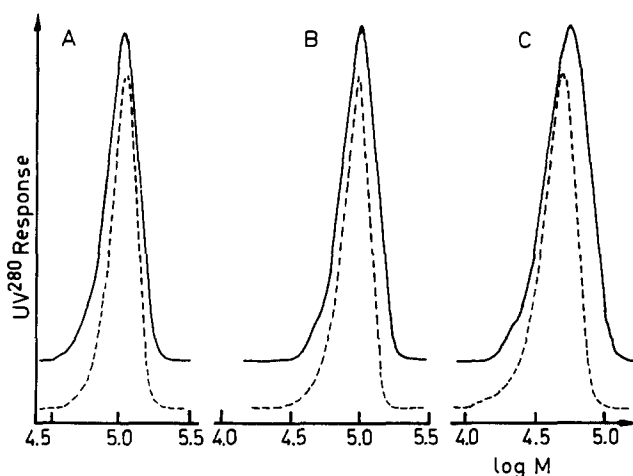


Figure 5 Chromatograms of the block copolymers (—) and the polystyrene precursors (---) at the critical point of PMMA; LiChrospher Si-300 and Si-1000, MEK-cyclohexane 70:30 vol%, flow rate 0.5 ml min^{-1} . (A) B1, P1; (B) B2, P2; (C) B3, P3; (D) B4; (E) B5

that only the PS and not the PMMA block gives a detector response.

Figure 5 shows the chromatograms of the block copolymers and their precursors, measured with a column system of silica gel Si-300 and Si-1000 and u.v. detection

Table 3 Molar-mass data from critical chromatography on a LiChrospher Si-300 and Si-1000 stationary phase, with polystyrene calibration

Sample	RI detection			U.v. detection ^a		
	M_n	M_w	U	M_n	M_w	U
P1	100 000	110 000	1.11	108 000	114 000	1.06
B1	104 000	117 000	1.12	111 000	119 000	1.07
P2	71 000	79 000	1.11	76 000	81 000	1.07
B2	73 000	87 000	1.18	85 000	91 000	1.07
P3	40 000	47 000	1.18	43 000	48 000	1.11
B3	45 000	59 000	1.31	54 000	61 000	1.13
B4				56 000	66 000	1.17
B5				4 000	8 000	1.89

^a At 280 nm

at 280 nm. Table 3 summarizes the quantitative results obtained via RI and u.v. (280 nm) detection. In all cases there is very good agreement between the molar masses of the block copolymers and the precursors. In addition, the data obtained for the precursors are in good agreement with the molar-mass values from the s.e.c. experiments. Comparing the molar masses and the polydispersities calculated from the RI and u.v. responses, a good agreement is obtained for the molar masses. In all cases the polydispersities calculated from the RI signal are gradually increased. This suggests that the influence of the PMMA block on the RI response cannot be neglected and the application of a selective detector is advisable. It is expected that the differences between RI and u.v. detection would be much more pronounced when block copolymers with a broad MMD and different MMDs of the separate blocks are investigated.

CONCLUSION

Chromatography at the critical point of adsorption has been shown to be a unique method for the analysis of diblock copolymers according to the MMD of the individual blocks. By operating at the critical point of one block, the other block may be analysed. Using this approach poly(styrene-*b*-methyl methacrylate)s were analysed according to the MMD of the polystyrene block. A comparison with data for the polystyrene precursors gave very good agreement, thereby proving the 'invisibility' concept.

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REFERENCES

- 1 Glöckner, G. 'Gradient HPLC of Copolymers and Chromatographic Cross-Fractionation', Springer, Berlin, 1991
- 2 Gorbunov, A. A. and Skvortsov, A. M. *Vysokomol. Soedin. (A)* 1988, **30**, 895
- 3 Gorbunov, A. A. and Skvortsov, A. M. *Vysokomol. Soedin. (A)* 1988, **30**, 453
- 4 Entelis, S. G., Evreinov, V. V. and Gorshkov, A. V. *Adv. Polym. Sci.* 1986, **76**, 129
- 5 Entelis, S. G., Evreinov, V. V. and Kuzaev, A. I. 'Reactive Oligomers', Khimiya, Moscow, 1988
- 6 Gorshkov, A. V., Evreinov, V. V. and Entelis, S. G. *Zh. Fiz. Khim.* 1985, **59**, 958
- 7 Pasch, H., Much, H., Schulz, G. and Gorshkov, A. V. *LC-GC Int.* 1992, **5**, 38
- 8 Pasch, H., Brinkmann, C., Much, H. and Just, U. *J. Chromatogr.* 1992, **623**, 315
- 9 Gankina, E., Belenkii, B. and Malakhova, I. *J. Planar Chromatogr.* 1991, **4**, 199
- 10 Zimina, T. M., Kever, J. J., Melenevskaya, E. Y. and Fell, A. F. *J. Chromatogr.* 1992, **593**, 233