# Chromatographic investigations of macromolecules in the critical range of liquid chromatography: 7. Analysis of the poly(methyl methacrylate) block in poly(styrene-*block*-methyl methacrylate)

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Poly(styrene-*block*-methyl methacrylate)s were analysed by liquid chromatography at the critical point of adsorption. Operating at chromatographic conditions, corresponding to the critical mode of polystyrene and a size exclusion mode for poly(methyl methacrylate), the molar mass and the polydispersity of the poly(methyl methacrylate) block in the block copolymers was determined. The chemical composition of the block copolymers was obtained using size exclusion chromatography with coupled density–refractive index detection, and compared to data calculated from critical chromatography experiments. The agreement of the data obtained by the different methods was found to be very good.

**(Keywords: block copolymers; liquid chromatography; critical range)**

## *Introduction*

The analysis of block copolymers is complicated, because they are characterized by distributions in molar mass and chemical composition. The determination of these distributions may be achieved by chromatographic cross-fractionation, where two different chromatographic techniques are coupled. One of these (usually size exclusion chromatography (s.e.c.)) provides information on the molar mass distribution and the other (gradient elution chromatography) yields the chemical composition[1].

Another, more recent, approach is the separation of heteropolymers at the critical point of adsorption of one of the components. This concept assumes that chromatographic conditions exist under which heteropolymers are 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 of telechelic oligomers and polymers[4–6].

As was shown for some applications, the 'invisibility' concept can be applied to the characterization of block copolymers[7–10]. For example, taking a block copolymer $A_nB_m$, the block $A_n$ may be regarded as the functional group or inhomogeneity. Therefore, operating at the critical point of $B_m$ the block $A_n$ may be analysed, and vice versa.

In the first part of this investigation, the polystyrene (PS) block of poly(styrene-*block*-methyl methacrylate)s was analysed with respect to its molar mass distribution, operating at chromatographic conditions, corresponding to the critical point of the poly(methyl methacrylate) (PMMA) block[11]. The present report is dedicated to the analysis of the PMMA block. Accordingly, chromatographic conditions have to be established, corresponding to the critical point of PS.

## *Experimental*

The critical chromatography experiments were carried out on a modular h.p.l.c. system, comprising a Waters model 510 pump, a Waters differential r.i. detector R401, a Knauer u.v./vis. filter photometer, a six-port injection valve and a Waters column oven. The columns were Macherey-Nagel Nucleosil 300-5 $C_{18}$ and 1000-7 $C_{18}$, 250 × 4 mm i.d. The flow rate was 0.5 ml $min^{-1}$, 20 μl of 0.5–1 wt% polymer solutions were injected. The column temperature was kept at 25°C for all experiments.

The instrumentation of the s.e.c. experiments with coupled density–refractive index detection was described in detail in a previous paper[12]. The column was Phenomenex Phenogel M.

The poly(styrene-*block*-methyl methacrylate)s were prepared by anionic polymerization. The procedure is described in part 4 of this series[11].

## *Results and discussion*

The critical point for the PMMA block of the block copolymers was established on silica gel LiChrospher Si-300 and Si-1000 as the stationary phase and

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methylethylketone (MEK)/cyclohexane 70/30 v/v as the eluent. Under these conditions the block copolymer was eluted in a size exclusion mode with respect to the PS block[11].

In agreement with the principles of liquid chromatography at the critical point of adsorption, the analysis of the PMMA block has to be conducted on a different chromatographic system. Similarly to the previous experiments, the PMMA block is to be analysed at the critical point of PS. Formally, the critical point for PS can be estalished on different stationary phases. Using a silica gel stationary phase, at the critical point of PS, PMMA would be eluted in an adsorption mode. As retention in the absorption mode is exponentially related to the molar mass, irreversible adsorption would be likely to occur for higher molar mass samples. Therefore, it is assumed to be more useful to carry out the separations on a stationary phase with reversed adsorption properties. In this case, retention will be directed by the hydrophobicity of the sample and accordingly, at the critical point of PS the block copolymer would be eluted in a size exclusion mode with respect to the PMMA block. A reversed stationary phase such as RP-18 is likely to provide a solution to this problem. A non-aqueous reversed phase system, comprising tetrahydrofuran (THF) and acetonitrile (ACN), was selected as the eluent. With respect to the molar mass region to be analysed, RP-18 columns with an average pore size of 300 and 1000 Å were combined.

The retention behaviour of PS on Nucleosil RP-18 is shown in *Figure 1*. When the mobile phase comprises only THF, normal size exclusion behaviour is obtained, i.e. retention time decreases with increasing molar mass of the sample. By adding ACN to the mobile phase, the slope of the calibration curve *M versus* retention time changes, indicating the transition from a pure size exclusion into a mixed size exclusion–adsorption mechanism. Enthalpic interactions with the stationary phase start to affect the retention behaviour, and at an eluent composition of THF/ACN 47/53 v/v these interactions become predominant and the retention behaviour corresponds to an adsorption mode.

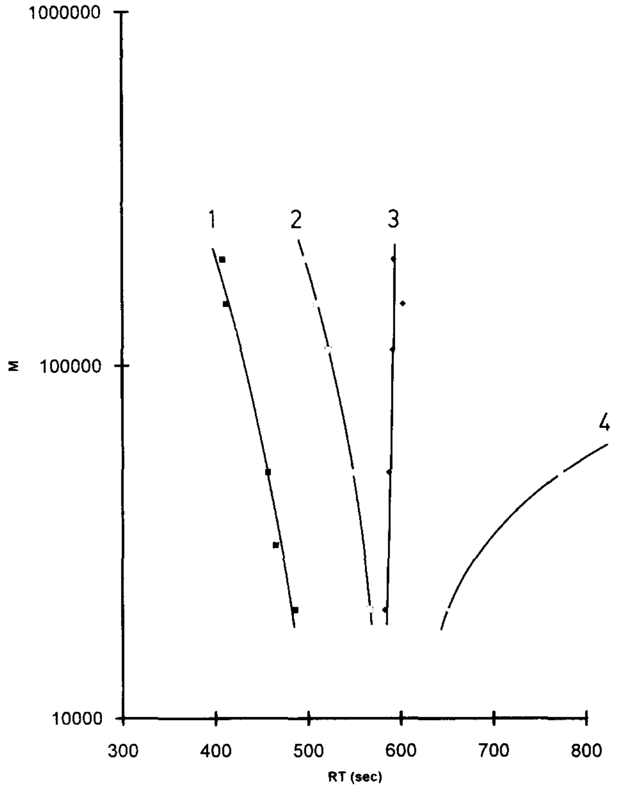

**Figure 1** Critical diagram of molar mass, *M*, *versus* retention time of PS. Stationary phase, Nucleosil RP-18 300+1000 Å; mobile phase, THF/ACN 100/0 (1), 50/50 (2), 49/51 (3) and 47/53 v/v (4)

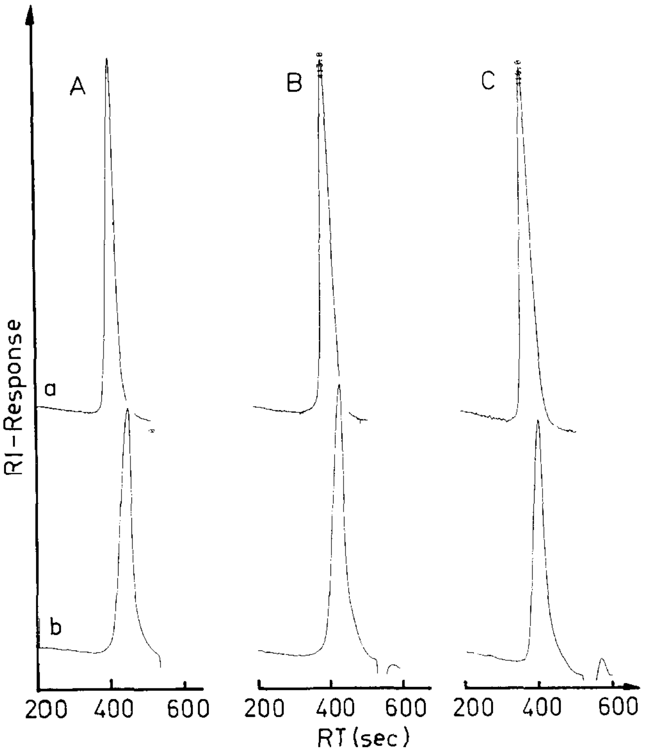

**Figure 2** Chromatograms of the block copolymers B1 (A), B2 (B) and B3 (C) in different chromatographic modes. Stationary phase, see *Figure 1*; mobile phase, THF/ACN 100/0 (a) and 49/51 v/v (b)

The transition point from size exclusion to the adsorption mode corresponds to an eluent composition of THF/ACN 49/51 v/v. This is the critical point of adsorption with respect to PS, where the entropic and enthalpic interactions of the macromolecules and the stationary phase exactly compensate each other, and the retention time becomes independent of the macromolecule size. On the other hand, these chromatographic conditions correspond to a size exclusion mode for PMMA. Accordingly, it is assumed that at the critical point of PS, the poly(styrene-*block*-methyl methacrylate)s are eluted exclusively with respect to the block length of the PMMA block and the PS block behaves like an invisible part of the macromolecule.

In *Figure 2* the chromatographic behaviour of the block copolymers in the size exclusion mode for both block components (100 vol% THF) and in the critical mode for the PS block (THF/ACN 49/51 v/v) is shown. In agreement with our assumption, at the critical point of PS the block copolymers are eluted at higher retention times, indicating lower molar masses. Accordingly, the retention of the block copolymers in the critical mode is not controlled by both block components but only by the PMMA block. Using an appropriate PMMA calibration curve, the molar mass and the polydispersity of the PMMA block in the block copolymers may be calculated.

**Table 1** Molar mass and polydispersity of the PMMA block in poly(styrene-*block*-methyl methacrylate). Stationary phase, RP-18-300+1000 Å; mobile phase, THF/ACN 49/51 v/v

| Sample | Nominal $M_w$(PMMA) | Determined $M_w$(PMMA) | Polydispersity |
|---|---|---|---|
| B1 | 55 000 | 49 000 | 1.32 |
| B2 | 89 000 | 97 000 | 1.49 |
| B3 | 133 000 | 143 000 | 1.36 |

**Table 2** Comparison of the total molar masses of the block copolymers determined using different methods

| Sample | Nominal[a] $M_w$ | S.e.c.[b] $M_w$ | S.e.c.[c] $M_w$ | Critical chromatography $M_w$(PS+PMMA) |
|---|---|---|---|---|
| B1 | 165 000 | 152 000 | 153 000 | 168 000 |
| B2 | 182 000 | 141 000 | 156 000 | 188 000 |
| B3 | 188 000 | 140 000 | 134 000 | 204 000 |

[a] S.e.c., light scattering detection
[b] Styragel, THF, PS calibration
[c] Silica gel, MEK, PS calibration

The results in *Table 1* show that the nominal and the determined weight-average molar masses of the PMMA blocks are of the same magnitude, as expected from the corresponding analysis of the PS block[11]. From the molar masses of the individual blocks the total molar masses of the block copolymers may be calculated. The comparison of these data, with results from conventional s.e.c. experiments, are summarized in *Table 2*. It can be seen that there is a very good agreement between the two s.e.c. methods. Compared to the nominal values, however, the molar masses are too low. For the determination of the nominal molar masses s.e.c. with light scattering detection was used, whereas for the two s.e.c. methods refractive index (r.i.) detection and a PS calibration were used. Due to the different hydrodynamic volumes of PS and PMMA for the same molar masses, this calibration is not fully appropriate and a mismatch of data is obtained. On the other hand, a very good agreement between the nominal molar masses and the critical chromatography values is obtained. This is a strong indication that using critical chromatography, the molar masses of the individual blocks may be determined and the total molar mass of the block copolymers may be calculated with high accuracy.

In order to compare the results of critical chromatography with the results of an independent method, s.e.c. with coupled density (*D*) and r.i. detection was used for the characterization of the block copolymers. In recent years, besides the conventional u.v. and r.i. detection in s.e.c., density detection has been introduced by Trathnigg and co-workers[13,14]. In particular, the coupled *D*-r.i. detection has been shown to be a useful method for the characterization of copolymers with respect to their chemical composition.

The molar mass distribution curves of the block copolymers and the mass distribution curves of the components, determined by s.e.c. with coupled *D*-r.i. detection, are shown in *Figures 3* and *4*. For the block copolymers B1 and B3 the mass distribution of the comonomers is very homogeneous. Only for B2 is a more heterogeneous mass distribution with respect to PS obtained. At the lower-molar-mass end of the distribution

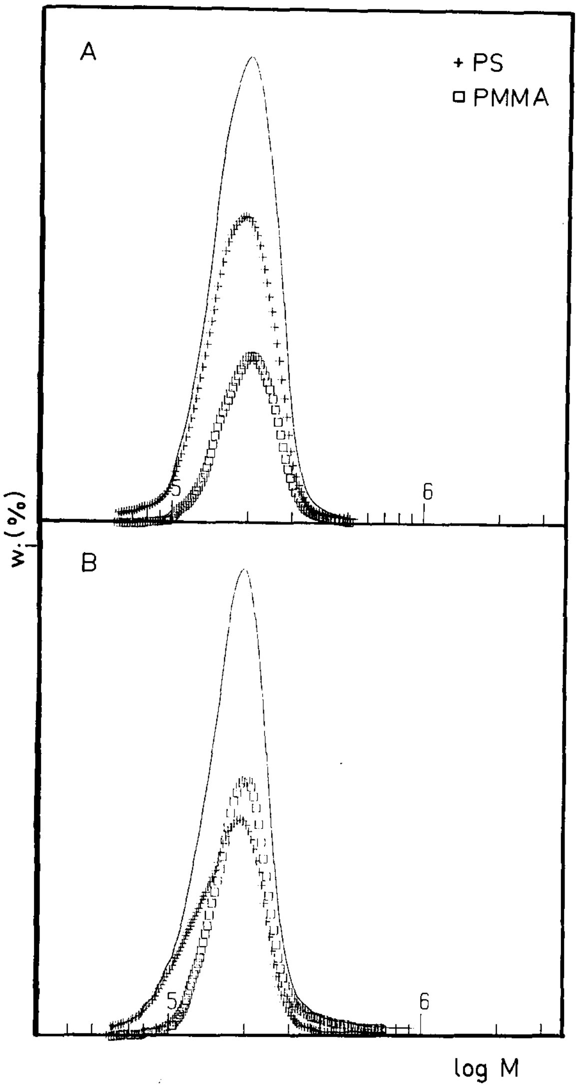

**Figure 3** Total mass distribution of the block copolymers B1 (A) and B2 (B) and separated distributions of the monomer units of the block copolymers from s.e.c. (*D*–r.i.). Stationary phase, Phenogel; mobile phase, chloroform

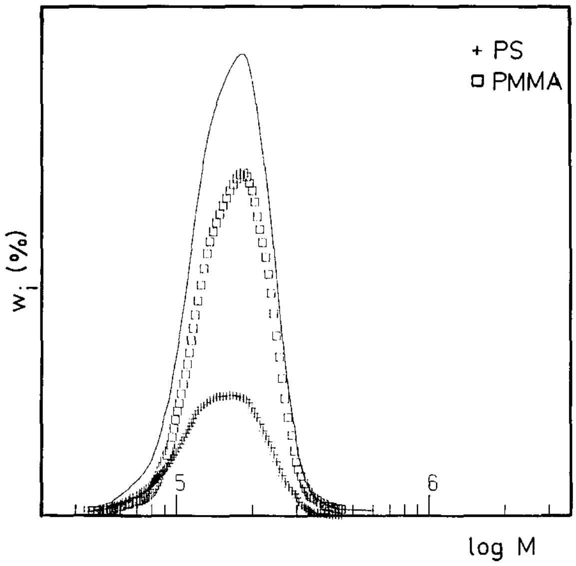

**Figure 4** Total mass distribution of the block copolymer B3 and separated distributions of the monomer units of the block copolymers from s.e.c. (*D*–r.i.). Stationary phase, Phenogel; mobile phase, chloroform

**Table 3** Chemical composition of the poly(styrene-*block*-methyl methacrylate)s determined by critical chromatography and s.e.c. with coupled *D*–r.i. detection (S/MMA in mol%)

| Sample | Nominal | Critical chromatography[a] | S.e.c. (*D*–r.i.) |
|---|---|---|---|
| B1 | 67/33 | 71/29 | 69/31 |
| B2 | 51/49 | 48/52 | 53/47 |
| B3 | 29/71 | 30/70 | 30/70 |

[a] Determined from the molar masses of the PS[11] and the PMMA blocks

curves, a certain amount of PS homopolymer seems to appear. Obviously, this PS homopolymer, which was formed in the first polymerization step, failed to continue the polymerization upon addition of the MMA monomer.

The chemical composition of the block copolymers is summarized in *Table 3*. As can be seen, excellent agreement between the different data sets is obtained. In this way, it is demonstrated that critical chromatography yields not only information on the block length of the individual blocks but also on the total chemical composition of the block copolymers.

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