

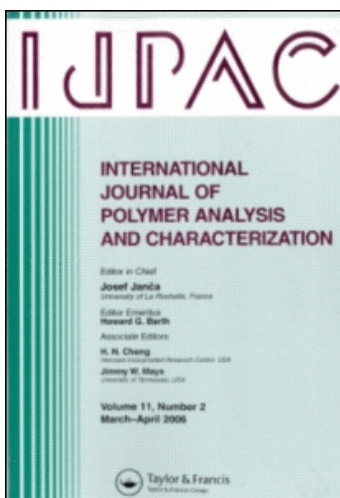
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D. Braun<sup>a</sup>; E. Esser<sup>a</sup>; H. Rasch<sup>a</sup>

<sup>a</sup> Deutsches Kunststoff-Institut, Darmstadt, Germany

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# Chromatographic Investigations of Macromolecules in the Critical Range of Liquid Chromatography. XII. Analysis of Block Copolymers of Styrene and Butadiene

D. BRAUN, E. ESSER and H. PASCH\*

*Deutsches Kunststoff-Institut, Schlossgartenstr. 6, 64289 Darmstadt, Germany*

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The separation of di- and triblock copolymers of styrene and butadiene was accomplished by liquid chromatography at the critical point of adsorption. The size of the polybutadiene blocks was determined under chromatographic conditions corresponding to the critical point of adsorption of polystyrene using silica gel as the adsorbent and tetrahydrofuran-hexane as the eluent. The polystyrene blocks were analyzed on a nonpolar stationary phase and methyl ethyl ketone-cyclohexane as the eluent, using chromatographic conditions, corresponding to the critical point of adsorption of polybutadiene. The deviations of the experimentally determined molar masses from the nominal values were discussed considering the complex structure of the block copolymers. For triblock copolymers with sharp transitions between the blocks, it was demonstrated that the block lengths of the outer, as well as the center blocks, can be determined with high accuracy by liquid chromatography at the critical point of adsorption. For di- and triblock copolymers with tapered transitions, the observed deviations are caused by the random sequences in the macromolecules.

*Keywords:* Liquid chromatography; Infrared spectroscopy; Polymer analysis; Styrene-butadiene block copolymers; Coupled techniques

## INTRODUCTION

The analysis of block copolymers by liquid chromatography at the critical point of adsorption (LCCC) is attractive since this technique

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\*Corresponding author.

provides selective information on the block lengths of the individual blocks. Different from any other liquid chromatographic technique, LCCC operates at conditions where only one block of a diblock copolymer is responsible for the retention behavior, while the other block is chromatographically “invisible”, i.e., does not contribute to retention.<sup>[1–5]</sup> The application of LCCC to block copolymers is based on the consideration that Gibbs free energy  $\Delta G_{AB}$  of a diblock copolymer  $A_nB_m$  is the sum of the contributions of block A and block B,  $\Delta G_A$  and  $\Delta G_B$ , respectively:

$$\Delta G_{AB} = \sum (n_A \Delta G_A + n_B \Delta G_B). \quad (1)$$

As specific interactions between blocks A and B are usually negligible in the chromatographic system, an interaction parameter  $\chi_{AB}$  must not be introduced in Equation (1).

With chromatographic conditions, corresponding to the critical point of homopolymer A, block A in the block copolymer will be chromatographically invisible, and the block copolymer will be eluted solely with respect to block B,  $K_d$  being the distribution coefficient:

$$\Delta G_A = 0, \quad (2a)$$

$$\Delta G_{AB} = n_B \Delta G_B, \quad (2b)$$

$$K_d^{AB} = K_d^B. \quad (2c)$$

At the critical point of homopolymer B, block B will be chromatographically invisible, and the block copolymer will be eluted solely with respect to block A:

$$\Delta G_B = 0, \quad (3a)$$

$$\Delta G_{AB} = n_A \Delta G_A, \quad (3b)$$

$$K_d^{AB} = K_d^A. \quad (3c)$$

The first evidence for the validity of this approach was given by Gankina *et al.*<sup>[6]</sup> for the analysis of block copolymers by thin layer chromatography. Column liquid chromatography was used by Zimina *et al.*<sup>[7]</sup> for the analysis of poly(styrene-block-methyl methacrylate) and

poly(styrene-block-*t*-butyl methacrylate). However, the critical conditions were established only for the polar part of the block copolymers, i.e., PMMA and PtBMA, respectively. Thus, only the polystyrene block was analyzed. The analysis of both blocks in diblock copolymers was presented by Pasch *et al.* for poly(styrene-block-methyl methacrylate)<sup>[8,9]</sup> and poly(decyl methacrylate-block-methyl methacrylate).<sup>[10,11]</sup>

According to Gorbunov and Skvortsov,<sup>[12]</sup> triblock copolymers of the ABA' type can be analyzed by LCCC similar to the analysis of diblock copolymers. The two possible cases for this type of investigation are (a) the analysis with respect to the inner block B using the critical conditions of the outer blocks A and A', and (b) the analysis of the outer blocks A and A' using the critical conditions of the inner block B. Skvortsov and Gorbunov<sup>[13]</sup> noted that it is necessary for the "invisible" block to be a free end. This would limit the method to the determination of the central block of triblock copolymers. It is believed that the LCCC concept cannot be used for the central block of triblock copolymers; however, this statement is not proven experimentally.

The separation of triblock copolymers of ethylene oxide (EO) and propylene oxide (PO), namely HO(EO)<sub>n</sub>(PO)<sub>m</sub>(EO)<sub>n</sub>OH, at the critical point of the EO outer blocks has been described by Gorshkov *et al.*<sup>[14]</sup> and Pasch *et al.*<sup>[15]</sup> At this point the EO blocks were chromatographically invisible, and the block copolymers were eluted with respect to the chain length of the inner PO block which was separated in the adsorption mode. Due to problems of solubility and specific interactions with the stationary phase, it was not possible to determine the outer EO blocks at the critical point of PPO.

The present investigation is dedicated to the analysis of di- and tri-block copolymers of styrene and butadiene. For the quantitative analysis of the polystyrene and the polybutadiene blocks, respectively, the critical conditions will be established for the corresponding homopolymers. At the critical point of polystyrene (PS) the polybutadiene block will be determined, while at the critical point of polybutadiene (PB) the PS block is to be analyzed. Since PB comprises a free end in the diblock copolymers and a center block in the triblock copolymers, it will be validated if LCCC is able to analyze the PB block correctly in both cases.

TABLE I Manufacturer's data on the styrene-butadiene block copolymers

Sample	Composition (weight fraction)	Random styrene (wt%)	$M_w$ (g/mol)	$M_n$ (g/mol)	$M_w/M_n$
1	PB(35)tPS(65)	12	108,000	100,000	1.08
2	PS(32.5)PB(35)PS(32.5)	0	105,000	99,000	1.06
3	PS(16)PB(35)PS(49)	0	108,000	102,000	1.06
4	PS(16)PB(35)tPS(49)	12	118,000	105,000	1.12
5	PS(16)PB(35)tPS(49)	23	112,000	101,000	1.11

t – tapered PB-PS link.

## EXPERIMENTAL

The separations were carried out on a modular chromatographic apparatus, comprising a Waters model 510 pump, a Waters 410 differential refractometer, a Waters 486 tunable UV detector, a Rheodyne six-port injection valve and a Waters column oven. The columns were either Merck LiChrospher Si-300 and Si-1000, 10- $\mu$ m average particle size, 200  $\times$  4 mm i.d., self-packed columns, or Macherey–Nagel Nucleosil 5C<sub>18</sub>, 300 Å + 1000 Å, 250  $\times$  4 mm i.d., prepacked columns. The experiments using coupled LCCC–FTIR were carried out using the LC Transform<sup>®</sup> (Lab Connections, Marlborough, USA).

All solvents were HPLC grade. The samples were technical products of BASF AG, Ludwigshafen, Germany. The compositions and molar masses given by the manufacturer are summarized in Table I.

## RESULTS AND DISCUSSION

Depending on the polarity of blocks A and B in block copolymers  $A_nB_m$ , and  $A_nB_mA_n$  and the polarity of the stationary phase, different chromatographic situations can be encountered. For example, at the critical point of homopolymer A, homopolymer B may be separated either in the SEC mode (case 1) or the adsorption mode (case 2). The same is true for the critical point of B, where A may be eluted according to SEC (case 3) or adsorption modes (case 4). Preferable, of course, are cases 1 and 3, whereas in the cases 2 and 4 for high-molar-mass polymers, irreversible adsorption may be encountered. Let us now consider that the polarity of A is higher than the polarity of B. In this

example, chromatographic behavior according to case 1 is achieved, when silica gel is used as the stationary phase (silica gel separates in the order of *increasing* polarity), while separation according to case 3 is obtained on a reversed phase, such as RP-8 or RP-18 (separation in the order of *decreasing* polarity).

The styrene-butadiene block copolymers under investigation were prepared by anionic polymerization of styrene and subsequent addition of butadiene for the diblock copolymer, and subsequent polymerization of styrene-butadiene-styrene for the triblock copolymers. As the PS block is the more polar block in the block copolymers, a polar (silica gel) column was chosen for establishing the critical point of PS. According to case 1 in the initial discussion, the PB block is then eluted in the SEC mode. The behavior of PS of different molar masses on silica gel in eluents, comprising tetrahydrofuran (THF) and *n*-hexane is shown in Figure 1.

Depending on the size of the macromolecules under investigation, similar to conventional SEC, the pore size of the stationary phase has to be adjusted to the desired molar mass region. Thus, for the present high-molar mass-samples, the investigations must be carried out on a column set with large pores, namely a two-column set of LiChrospher

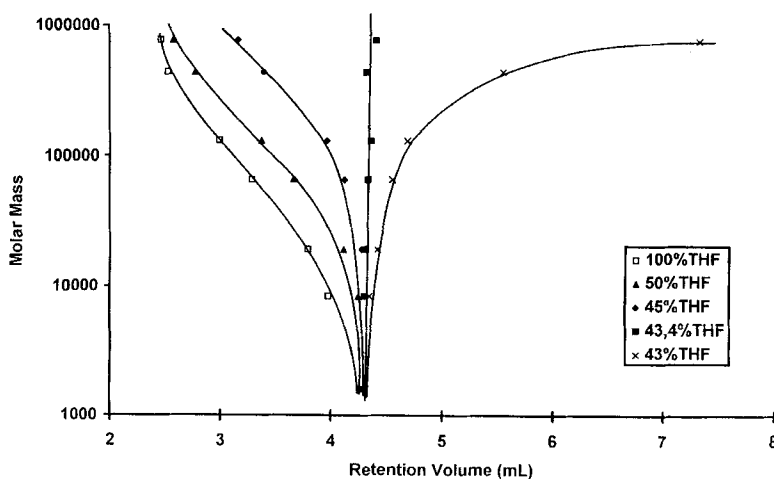


FIGURE 1 Critical diagram retention volume vs. molar mass of polystyrene; stationary phase: LiChrospher Si-300 + Si-1000; mobile phase: THF/*n*-hexane.

Si-300 and Si-1000 with pore sizes of 300 and 1000 Å, respectively. At concentrations of THF > 45% by volume, the SEC mode is operating, whereas at concentrations < 43% by volume of THF adsorption takes place. The critical point of PS is obtained at an eluent composition of THF/*n*-hexane 43.4% : 56.6% by volume, all PS samples being eluted in one peak. At this eluent composition, PB is eluted in the SEC mode. In agreement with theory, the elution zones of PS and PB are completely separated irrespective of the molar mass, see Figure 2.

The block copolymers under investigation exhibit different types of transition between the PB and PS blocks. In samples 2 and 3 there are sharp transitions between PS and PB (a), while in samples 1, 4, and 5 the transitions are tapered (b):

(a) ----BBBBB-SSSSSS-----

(b) ----BBBBB---BSBBSBSS---SSSSSS-----

A tapered transition is obtained when residual butadiene monomer is in the reaction mixture upon starting the formation of the PS block. In this case random styrene–butadiene sequences are formed until all

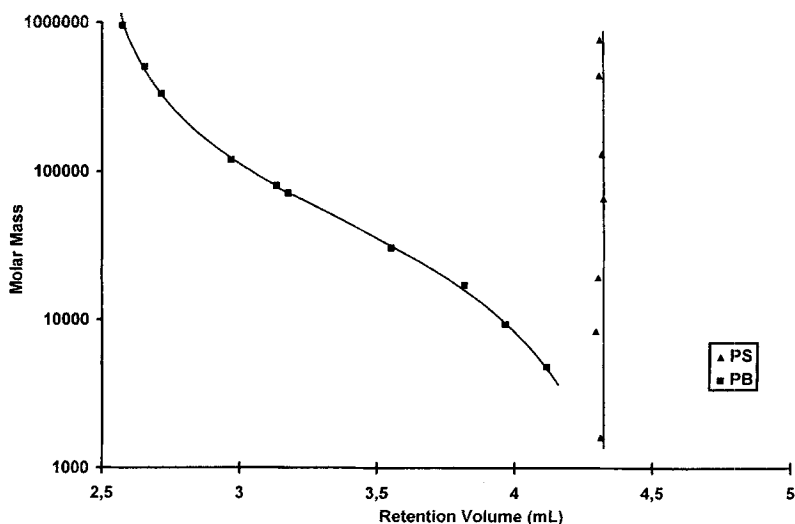


FIGURE 2 Calibration curves of polystyrene and polybutadiene at the critical point of polystyrene; stationary phase: LiChrospher Si-300 + Si-1000; mobile phase: THF/*n*-hexane 43.4% : 56.6% by volume.

butadiene is consumed. The amount of this random copolymer sequence is given by the weight fraction of "random styrene", 12% random styrene meaning that 12 wt% of the total styrene is located in the random copolymer, while 88 wt% is consumed in the formation of the PS block.

The chromatograms of samples 1, 2, and 4 are given in Figure 3. Similar to these chromatograms, for all samples under investigation one major elution peak at an elution volume of about 3.5 mL is obtained together with a minor peak at about 4.5 mL. Obviously, the

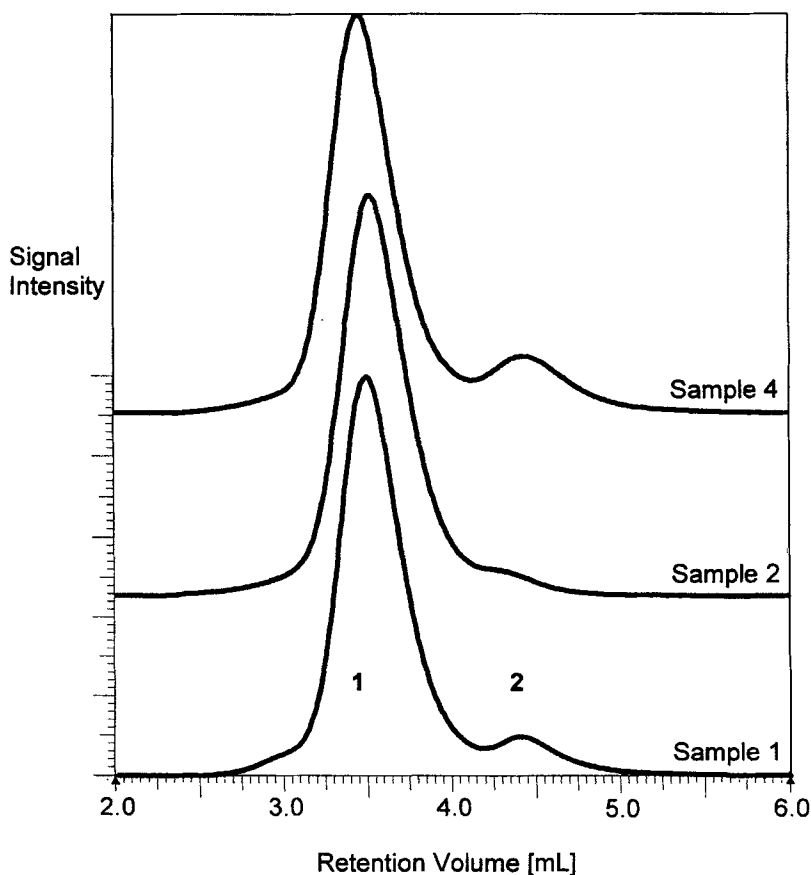


FIGURE 3 LCCC chromatograms of samples 1, 2, and 4 at the critical point of polystyrene, for chromatographic conditions see Figure 2.



major peak corresponds to the block copolymer, while the minor peak elutes at the same elution volume as polystyrene homopolymer. Since the polymerization was always started with styrene, it is possible that a certain fraction of the reactive polystyrene precursor deactivates before forming the PB block. In this case, a certain amount of PS homopolymer is encountered in the final product.

For determining the chemical composition of both peaks, LCCC is combined with FTIR spectroscopy via the LC Transform<sup>(b)</sup>. The design concept of the interface is briefly described.<sup>[16–18]</sup> The system is composed of two independent modules, the sample collection module and the optics module. The effluent of the liquid chromatography column is split with a fraction (frequently 10% of the total effluent) going into the heated nebulizer nozzle located above a rotating sample collection disc. The nozzle rapidly evaporates the mobile phase while depositing a tightly focused track of the solute. When a chromatogram has been collected on the sample collector disc, the disc is transferred to the optics module in FTIR for analysis of the deposited sample track. A control module defines the sample collection disc position and rotation rate in order to be compatible with the run time and peak resolution of the chromatographic separation. As a result, a complete FTIR spectrum for each position on the disc and, hence, for each sample fraction is obtained. This spectrum bears information on the chemical composition of each sample fraction. The set of all spectra can be arranged along the elution volume axis and yields a three-dimensional plot in the coordinates elution volume vs. FTIR frequency vs. absorbance. The projection of the three-dimensional plot on the elution volume-FTIR frequency coordinate system yields a two-dimensional representation (“contour plot”), where the intensities of the absorption peaks are given by a color code.

Such a contour plot readily provides information on the chemical composition of each chromatographic fraction, see Figure 4 for sample 4. Both components 1 and 2 are recognizable by their absorption peaks which can be used for structure elucidation. Obviously in both elution peaks PS is present, indicated by the characteristic absorptions at 699 and 758  $\text{cm}^{-1}$ . The presence of the polybutadiene block is indicated by the characteristic absorption peak at 966  $\text{cm}^{-1}$ . This absorption peak appears very strongly in component 1, while, in component 2, it is not present. Accordingly, elution peak 1 is due to the PS–PB–PS block

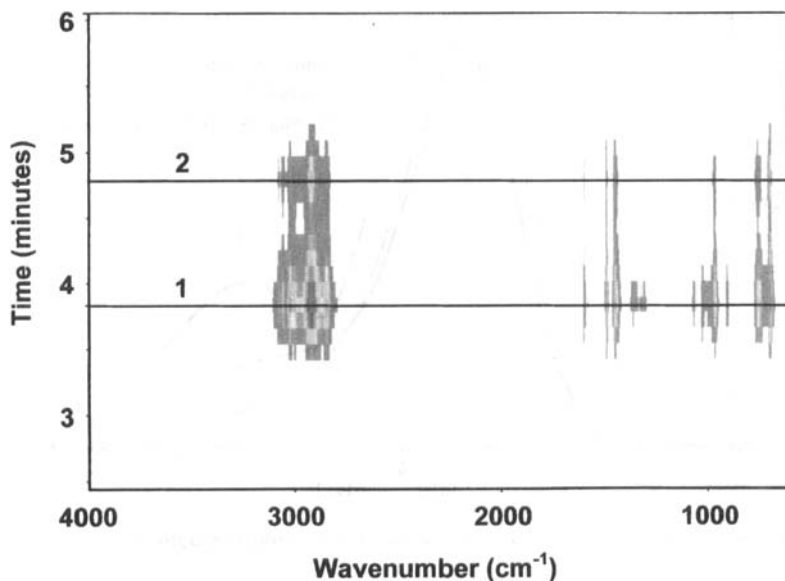


FIGURE 4 Contour plot of sample 4, for chromatographic conditions see Figure 2. (See color plate I.)

copolymer, while elution peak 2 indicates PS homopolymer as a by-product. An even more obvious presentation of the distribution of PS and PB along the elution peaks is given by the selective *chemigrams*, presented in Figure 5. Measuring the elution profile at the absorption frequency of PS ( $705\text{--}695\text{ cm}^{-1}$ ), elution peaks 1 and 2 are obtained similarly to Figure 3. When the elution profile is measured at the absorption frequency of PB ( $970\text{--}960\text{ cm}^{-1}$ ), however, only elution peak 1 is obtained, indicating that PB is not present in elution peak 2. This is a clear evidence of PS homopolymer constituting elution peak 2.

The present separations are carried out under chromatographic conditions, corresponding to the critical point of adsorption of PS. According to the theory, the block copolymers should behave like the PB center block since the PS outer blocks are chromatographically “invisible” under these conditions. It should then be possible to determine the chain length of the PB block irrespective of the PS blocks via a conventional PB calibration curve, see Figure 2. The calculated molar masses of the PB blocks, as compared to the nominal values

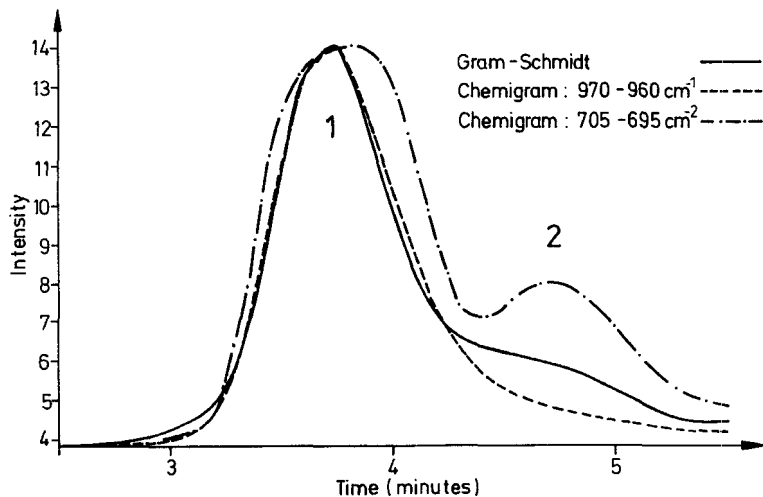
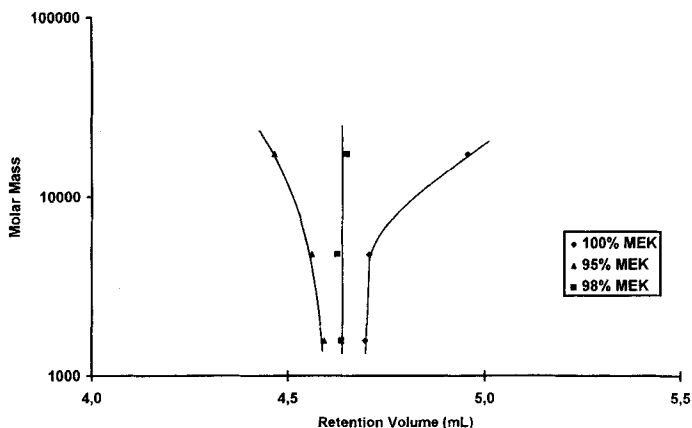


FIGURE 5 Selected *chemigrams* of sample 4, for chromatographic conditions see Figure 2.

calculated from the gross composition of the block copolymers, are presented in Table II. The best fit between the nominal and the experimental values is obtained for samples 2, 3 and 4, while samples 1 and 5 show a deviation of about 11% from the nominal values. This deviation can arise from improper determination of the gross composition or from an influence of the block copolymer structure. Samples 1, 4 and 5 contain a certain amount of random copolymer. The influence of this random fraction on the elution behavior cannot be estimated exactly, however, it must be assumed that this part does not behave "critically". From our experience we know that under the present chromatographic conditions random copolymers elute at higher elution volumes compared to block copolymers of the same composition. By the use of the same PB calibration curve for both, this would mean lower calculated molar masses for the random copolymers. If the same effect were operating for block copolymers containing a random part, the calculated molar masses should also be shifted to lower values, which is the case for samples 1 and 5. Unfortunately, the magnitude of this effect cannot be estimated, however, a deviation of only 11% from the nominal values is rather low and LCCC can be assumed to give a good estimate of the PB block size.

TABLE II Molar masses of the individual blocks in the styrene-butadiene block copolymers determined by LCCC

Sample	Composition PB/PS <sub>1</sub> /PS <sub>2</sub> (wt%)	$M_w$ (PB, calc.) (g/mol)	$M_w$ (PB, exp.) (g/mol)	$M_w$ (PS, calc.) (g/mol)	$M_w$ (PS, exp.) (g/mol)
1	35/65	37,800	33,600	70,200	76,800
2	35/32.5/32.5	36,700	36,200	68,300	71,800
3	35/16/49	37,800	37,300	70,200	71,600
4	35/16/49	41,300	40,600	76,700	85,800
5	35/16/49	39,200	35,200	72,800	83,000

FIGURE 6 Critical diagram retention volume vs. molar mass of polybutadiene; stationary phase: Nucleosil 5C<sub>18</sub> 300 + 1000; mobile phase: MEK/cyclohexane.

The analysis of the polystyrene blocks in the copolymers has to be conducted on a different chromatographic system. At the critical point of adsorption for PB, PS would elute in the SEC mode. Following our initial discussion, a nonpolar stationary phase must be used to accommodate conditions, where the more polar PS is eluted before the less polar PB. Initial tests of different mobile phases showed that for a number of solvent combinations PB becomes insoluble before reaching the critical point of adsorption. A suitable solvent combination appears to be methyl ethyl ketone (MEK)/cyclohexane, where PB exhibits typical SEC behavior in pure cyclohexane, while eluting in a weak adsorption mode in pure MEK. The critical point of adsorption on a RP-18 stationary phase corresponds to a mobile phase composition of MEK/cyclohexane 98%:2% by volume, see Figure 6. A limitation of this

phase system is that at critical conditions PB is soluble only up to molar masses of about 30,000 g/mol.

For the block copolymers under investigation, solubility problems are not encountered. Due to the good solubility of PS in MEK/cyclohexane, the block copolymers are soluble as well. The chromatograms of samples 2, 3 and 4 are presented in Figure 7. As expected from the nominal molar masses of the PS blocks, the major elution peak

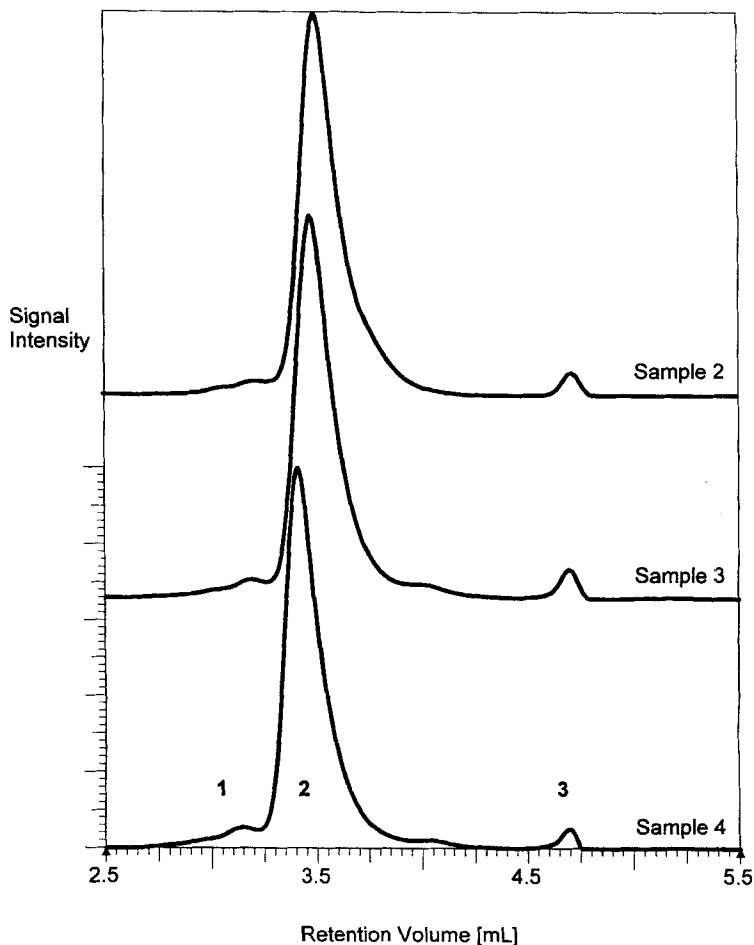


FIGURE 7 LCCC chromatograms of samples 2, 3 and 4 at the critical point of polybutadiene, stationary phase: Nucleosil 5C<sub>18</sub> 300+1000; mobile phase: MEK/cyclohexane 98%:2 vol%.

(peak 2) corresponding to the block copolymer fraction appears at similar elution volumes of about 3.5 mL for all samples. In addition, minor elution peaks are obtained at about 3.2 mL (peak 1) and 4.7 mL (peak 3). The elution volume of peak 3 corresponds to the critical elution volume of PB and, therefore, an LCCC-FTIR experiment is carried out for verification. Figure 8 shows the result of the coupling experiment as a *chemigram* representation for sample 3. The Gram-Schmidt curve results from a summation of all absorption peaks and shows the true concentration profile, while the *chemigrams* at 710–690 and 970–960  $\text{cm}^{-1}$  are selective for PS and PB, respectively. Due to the very low concentration of peak 3, the *chemigrams* do not provide suitable information; however, when the ratio of PB/PS is calculated from the *chemigrams*, the resulting curve clearly indicates the presence of PB in peak 3. For more evidence, sample 3 was mixed with a small amount of PB and the LCCC-FTIR experiment was repeated. As can be seen in Figure 9, the same elution profile is obtained showing the PB peak at the same position as peak 3 in Figure 8.

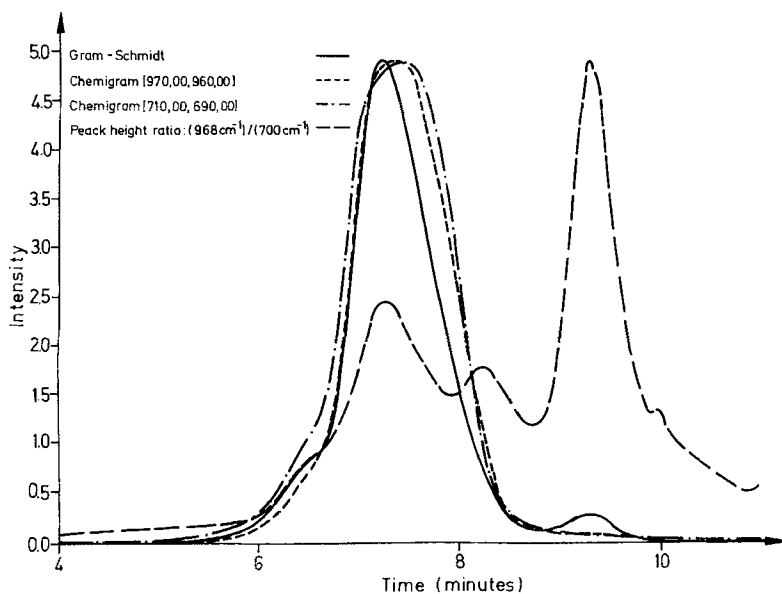


FIGURE 8 Selected *chemigrams* of sample 3, for chromatographic conditions see Figure 7.

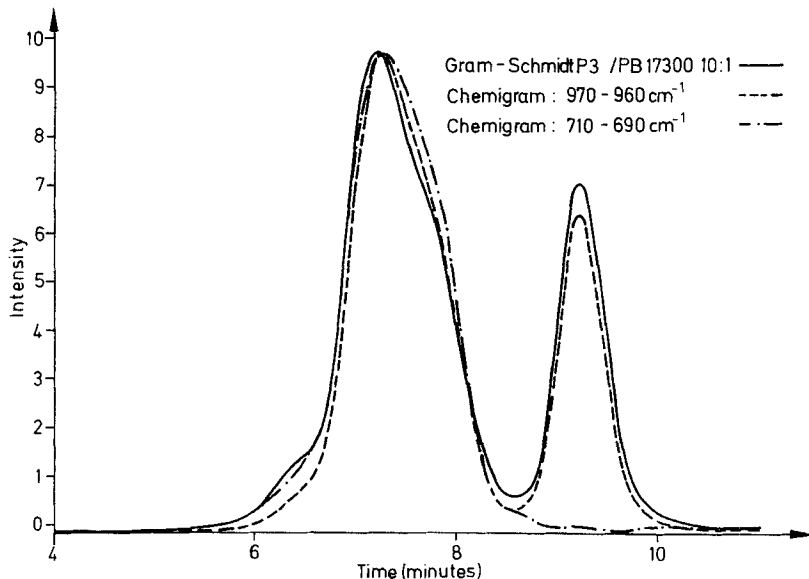


FIGURE 9 Selected *chemigrams* of a mixture of sample 3 and polybutadiene (17,300 g/mol), for chromatographic conditions see Figure 7.

For peak 1, the LCCC-FTIR experiment indicates the presence of PS and PB. Accordingly, this peak is due to a higher molar mass fraction of the copolymer which could result from the formation of a small fraction of multiblock copolymer. The calculation of the molar masses of the PS blocks of the block copolymers was carried out using a conventional PS calibration curve. The obtained data are summarized in Table II. A comparison with the PS molar masses calculated from the gross composition shows excellent agreement between calculated and experimental values for samples 2 and 3. This is expected since these samples exhibit sharp transitions between the PS and PB blocks. For the samples with tapered transitions, similar to the investigations at the critical point of PS, a certain deviation from the calculated values is obtained, which has again a magnitude of 10–13%. The deviations of the molar masses from the calculated values for the tapered block copolymers are roughly of the same magnitude as “random styrene”. It could, therefore, be assumed that the molar mass

deviations are a measure of the randomness of the polystyrene block. This assumption, however, needs further verification.

It is interesting that for the PB block, a negative deviation from the calculated value is obtained, while for the PS blocks the deviation is positive. One possible reason for this effect could be the composition of the random part. The random fraction results from the copolymerization of a small residue of butadiene and a large amount of styrene. It can, therefore, be assumed that the concentration of styrene units in the random fraction is much higher than the concentration of the butadiene units and the random fraction behaves more like PS. If this is the case, then at critical conditions of PS the random fraction shifts the elution peak of the block copolymer to higher retention volumes and, hence, lower calculated molar masses. At critical conditions of PB the opposite effect is obtained: the "PS-like" random fraction adds to the PS blocks, thus giving rise to a positive deviation of the molar masses.

From the molar masses of the individual blocks the average molar masses and gross compositions of the block copolymers can be calculated. As can be seen in Table III, the best fit is obtained for samples 2 and 3, while for the tapered samples 1, 4 and 5 less accurate results are obtained. However, in all cases the maximum deviation from the calculated data is less than 8%. Comparing the amount of information obtained by the LCCC experiments with what is obtainable by SEC or LAC, LCCC seems to be the better choice. For samples with sharp transitions between the blocks, LCCC yields accurate quantitative results for the center as well as for the outer blocks in triblock copolymers.

TABLE III Comparison of nominal and experimental molar masses and gross compositions for the styrene-butadiene block copolymers

Sample	Composition (wt%)		$M_w$ (g/mol)	
	Nominal PS/PB	From LCCC PS/PB	Nominal	From LCCC PS + PB
1	65/35	69/31	108,000	110,400
2	65/35	66/34	105,000	108,000
3	65/35	66/34	108,000	108,900
4	65/35	68/32	118,000	126,000
5	65/35	70/30	112,000	118,200



## CONCLUSION

LCCC coupled to FTIR spectroscopy has been shown to be an excellent method for the analysis of styrene–butadiene block copolymers. Different from any other technique, this combination method yields quantitative information on the chain lengths of the single blocks and the chemical compositions of the block copolymers. Future work will focus on the analysis of blends comprising styrene–butadiene and polybutadiene rubbers which are typically used in tire materials.

## Acknowledgment

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