Analytical Techniques for Polymers with Complex Architectures

Harald Pasch

Deutsches Kunststoff-Institut, Schloßgartenstr. 6, 64289 Darmstadt, Germany
E-mail: hpasch@dki.tu-darmstadt.de

SUMMARY: Complex polymers are distributed in more than one direction of molecular heterogeneity. In addition to the molar mass distribution, they are frequently distributed with respect to chemical composition, functionality, and molecular architecture. For the characterization of the different types of molecular heterogeneity it is necessary to use a wide range of analytical techniques. Preferably, these techniques should be selective towards a specific type of heterogeneity. The combination of two selective analytical techniques is assumed to yield a two-dimensional information on the molecular heterogeneity. For the analysis of complex polymers different liquid chromatographic techniques have been developed, including size exclusion chromatography (SEC) separating with respect to hydrodynamic volume, and liquid adsorption chromatography (LAC) which is used to separate according to chemical composition. Liquid chromatography at the critical point of adsorption (LC-CC) has been shown to be a versatile method for the determination of the functionality type distribution of macromonomers, the molecular architecture of homopolymers and the chemical heterogeneity of block and graft copolymers.
The present paper presents the principle ideas of combining different analytical techniques in multidimensional analysis schemes for the analysis of polymers with complex architectures. Branched block and graft copolymers can efficiently be analyzed with respect to chemical composition and molar mass by LC-CC and two-dimensional chromatography. The chemical heterogeneity as a function of molar mass can be determined by combining interaction chromatography and FTIR spectroscopy. For the analysis of star-like polymers LC-CC is shown to be a powerful technique when the molar mass of different segments (blocks, grafts) must be determined.

Introduction

Synthetic polymers are highly complex multicomponent materials. They are composed of macromolecules varying in chain length, chemical composition, and architecture. By definition, complex polymers are heterogeneous in more than one distributed property (for example, linear copolymers are distributed in molar mass and chemical composition). Depending on the composition of the monomer feed and the polymerization procedure, different types of heterogeneities may become important. For example, in the synthesis of tailor-made polymers frequently telechelics or macromonomers are used. These oligomers or polymers usually contain functional groups at the polymer chain end. Depending on the

 CCC 1022-1360/00/$ 17.50+.50/0

preparation procedure, they can have a different number of functional endgroups, i.e. be mono-, bifunctional etc. In addition, polymers can have different architectures, i.e. they can be branched (star- or comb-like), and they can be cyclic.

Different from low molar mass organic samples, where single molecules are to be determined, for complex synthetic polymers the analytical task is the determination of a distributed property. The molecular heterogeneity of a certain complex polymer can be presented either in a three-dimensional diagram or a so-called "contour plot". For a random copolymer these presentations are given in Figure 1.

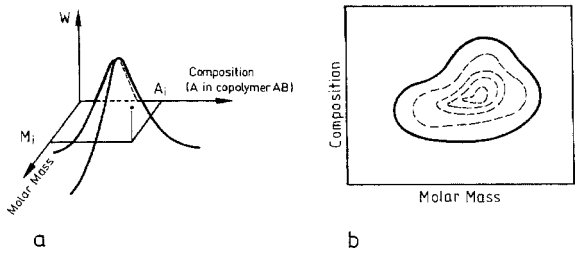


Fig. 1: Schematic representation of the molecular heterogeneity of a random copolymer in a 3D diagram (a) and a contour plot (b) [1)]

For copolymers, in particular random copolymers, a continuous drift in composition is characteristic. To determine this chemical composition drift in correlation with the molar mass distribution, a variety of analytical techniques must be used, including chromatographic separation combined with spectroscopic detection.

Another most efficient approach is the chromatographic separation of complex polymers by combining different separation mechanisms. A possible separation protocol for a complex polymer mixture is presented in Fig. 2. The sample under investigation comprises molecules of different chemical compositions (different colours) and different sizes. In a first separation step this mixture is separated according to composition yielding fractions which are chemically homogeneous. These fractions are transfered to a size-selective separation method and analysed with respect to molar mass. As a result of this two-dimensional separation, information on both typs of molecular heterogeneity is obtained.

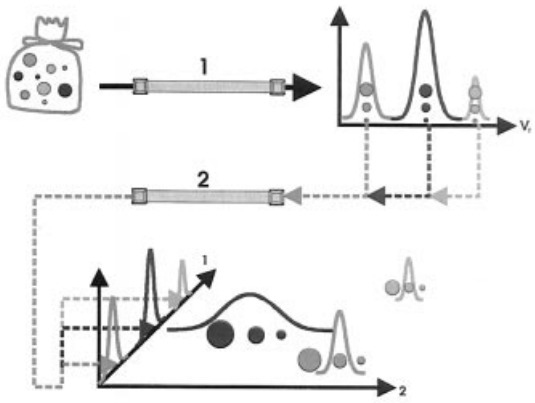


Fig. 2: Schematic separation protocol for the analysis of a complex polymer mixture [1)]

Two-dimensional Chromatography

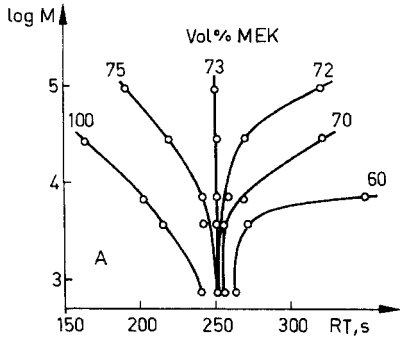
By the use of different modes of liquid chromatography it is possible to separate polymers selectively with respect to hydrodynamic volume (molar mass), chemical composition or functionality. Using these techniques and combining them with each other or with a selective detector, two-dimensional information on different aspects of molecular heterogeneity can be obtained. If, for example, two different chromatographic techniques are combined in a "cross-fractionation" mode, information on chemical composition distribution (CCD) and molar mass distribution (MMD) can be obtained.

One of the very selective modes of liquid chromatography of polymers is liquid chromatography at the critical point of adsorption (LC-CC) [2-4)]. LC-CC relates to a chromatographic situation, where the entropic and enthalpic interactions of the macromolecules and the column packing compensate each other. To describe this phenomenon the term "chromatographic invisibility" is used, meaning that the chromatographic behaviour is not directed by the size but by the inhomogeneities (chemical structure) of the macromolecules. Under such chromatographic conditions it is possible to determine the heterogeneities of the polymer chain selectively and without any influence of the polymer chain length. LC-CC has been successfully used for the determination of the

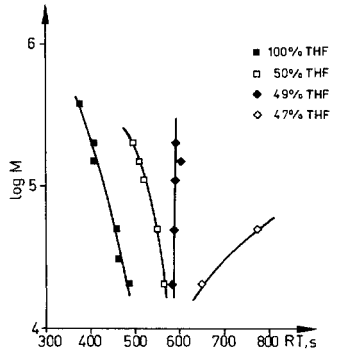
functionality type distribution of telechelics and macromonomers, for the analysis of block copolymers, macrocyclic polymers, and polymer blends [5,6].

Thus, LC-CC represents a chromatographic separation technique yielding fractions which are homogeneous with respect to chemical composition but distributed in molar mass. These fractions can readily be analysed by SEC which for chemically homogeneous fractions provides true molar mass distributions without interference of CCD or functionality type distribution (FTD). Therefore, the combination of LC-CC and SEC in a 2D set-up can truely be regarded as "orthogonal" chromatography provided that LC-CC comprises the first dimension [7]. Consequently, for copolymers being distributed in chemical composition and molar mass, coupled LC-CC vs. SEC can yield combined information on CCD and MMD. This type of dual information is of significant importance, for example, for detailed structural analysis of block copolymers [8,9].

Using LC-CC, block copolymers of styrene and methyl methacrylate can be analysed with regard to the molar mass of the individual blocks and the presence of homopolymer. For such an analysis, the critical points for the homopolymers PS and PMMA must be determined. As can be seen in Fig. 3, the critical point for PS is obtained on a RP-18 stationary phase, while the critical point for PMMA is established on a silica gel stationary phase.



(A) Critical Conditions for PMMA silica gel, MEK-cyclohexane



(B) Critical Conditions for PS RP-18, THF-ACN

Fig. 3: Critical diagrams for PMMA (A) and polystyrene (B) [8,9]

The chromatographic separation of a PS-b-PMMA block copolymer under critical conditions for PS is shown in Fig. 4. The block copolymer and residual PS precursor give separate chromatographic peaks which can be quantified. Using a PMMA calibration curve, the molar of the PMMA block in the block copolymer can be determined.

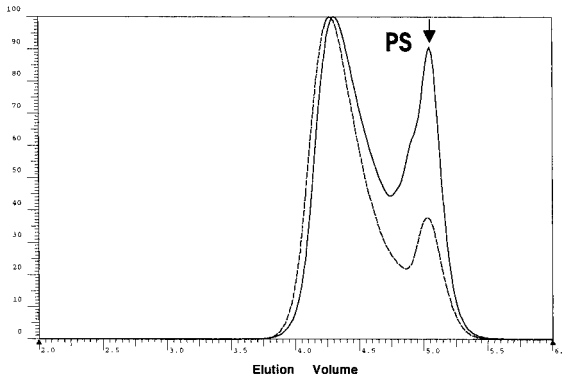


Fig. 4: LC-CC separation of a PS-b-PMMA block copolymer, first peak: PS-b-PMMA, second peak: PS precursor, detectors: RI (- - - -) and UV (——)

Information on chemical composition as a function of molar mass is obtained by coupling the LC-CC separation to SEC in an on-line 2D chromatography setup. The resulting contour plot CCD vs. MMD yields quantitative information on the molar masses of both the block copolymer and the PS homopolymer, their amounts and the molar mass of the PMMA block, see Fig. 5.

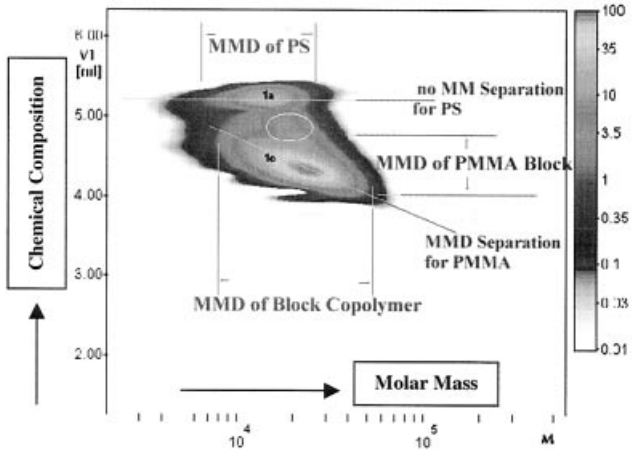


Fig. 5: 2D separation LC-CC vs. SEC of a PS-b-PMMA block copolymer

By combining different techniques of interaction chromatography with SEC in two-dimensional chromatography, a large variety of polymers with complex architectures can be analysed. The separation of the crude product of a grafting reaction of methyl methacrylate onto polybutadiene (PB) by 2D chromatography is shown in Fig. 6. In this case, gradient HPLC is used in the first dimension.

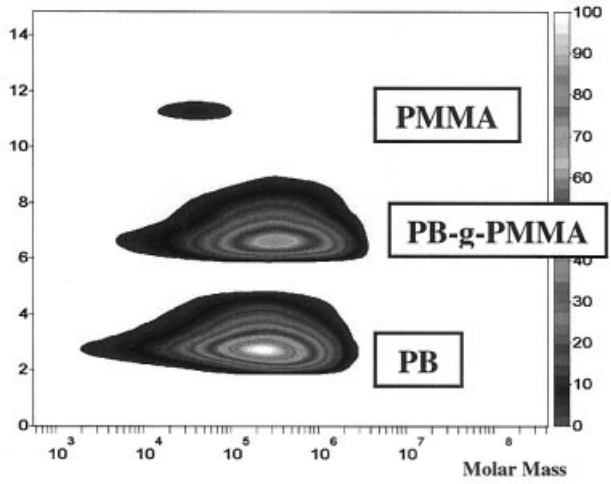


Fig. 6: 2D separation gradient HPLC vs. SEC of a PB-g-PMMA graft copolymer

As can be seen, the product consists of the graft copolymer PB-g-PMMA, residual non-grafted PB and PMMA homopolymer. The quantitative analysis for two different reaction products is given in Table 1. Additional information on the chemical composition of the graft copolymer can be obtained by coupling the gradient HPLC separation to FTIR spectroscopy.

Table 1: Quantitative analysis of graft products by 2D chromatography

Reaction Time [h]	**Component**	**M_w**	**Amount [%]**
1	PB	278.600	52
	PB-g-PMMA	405.100	44
	PMMA	33.400	1
4	PB	247.400	31
	PB-g-PMMA	686.600	64
	PMMA	32.600	4

Hyphenation of Liquid Chromatography with Spectroscopic Methods

The determination of compositional changes across the molar mass distribution of a polymer or the detection of a specific component in a complex polymer mixture is of considerable interest. This information allows to predict physical properties and ultimately the performance of the polymer. Several analytical techniques are of use in determining these properties. Mass spectrometry, NMR, and infrared spectroscopy can be used to provide data about the compositional details of the sample.

The direct coupling of HPLC and FTIR spectroscopy is possible by using the LC-Transform interface of Lab Connections. The design concept of the interface is shown in Fig. 7.

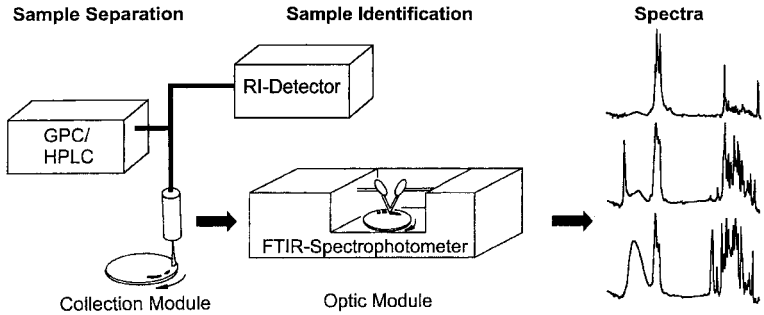


Fig. 7: Schematic representation of coupled liquid chromatography and FTIR spectroscopy [1)]

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 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 the 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. Data collection is readily accomplished with software packages presently used for GC-FTIR. The sample collection disc is made from germanium which is optically transparent in the range 6000-450 cm^{-1}. The lower surface of the disc is covered with a reflecting aluminum layer. As a result of the investigation a complete FTIR spectrum for each position on the disc and, hence, for each sample fraction is

obtained [10,11]. This spectrum bears information on the chemical composition of each sample fraction. The set of all spectra can be arranged along the elution time axis and yields a three-dimensional plot in the coordinates elution time-FTIR frequency-absorbance.

The analysis of the chemical composition of a binary polymer blend by coupled SEC-FTIR using the LC Transform is shown in Fig. 8. After separating the sample with respect to molecular size, the fractions were deposited on the germanium disc and FTIR spectra were recorded continuously along the sample track. In total, a set of about 80 spectra was obtained which can be presented in a three-dimensional plot. The projection of the 3D plot on the retention time-IR frequency coordinate system yielded a two-dimensional representation, where the intensities of the absorption peaks were given by a colour code. Such a contour plot readily provides information on the chemical composition of each chromatographic fraction. It was obvious that the chromatographic peaks 1 and 2 had different chemical structures. By comparison with reference spectra which are accessible from corresponding data bases, component 1 could be identified as polystyrene, while component 2 was polyphenylene oxide.

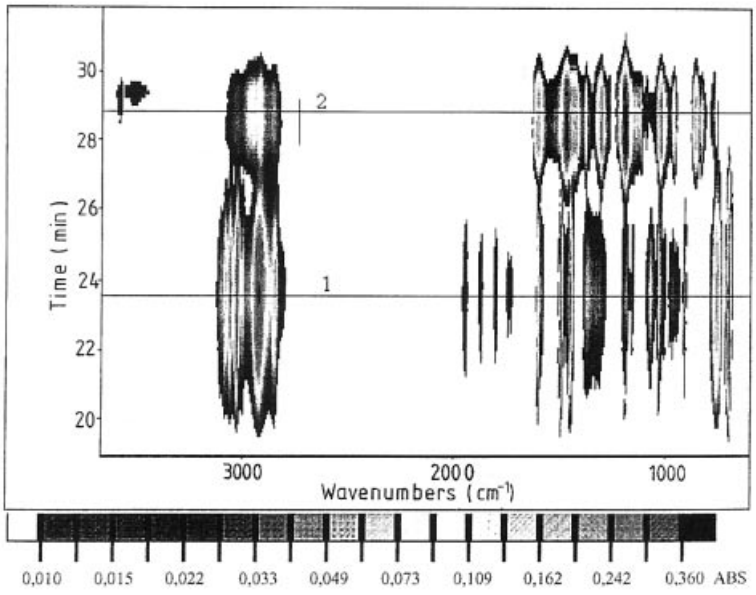
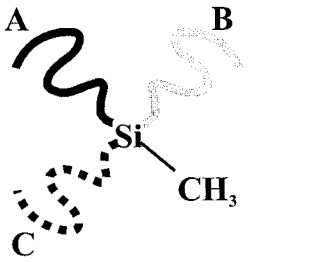


Fig. 8: SEC-FTIR analysis of a binary blend, contour plot representation

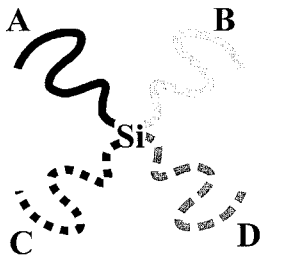
This type of analysis can be conducted for virtually every type of polymer, provided that an liquid chromatographic separation can be done. As the LC mode, SEC, LC-CC, gradient HPLC or any other mode of liquid chromatography can be used.

Analysis of Star Polymers

During the last years a number of well-defined miktoarm star (μ-star) polymers have been synthesized using the chlorosilane approach. Miktoarm star polymers are star-shaped block copolymers where chemically different homopolymers constitute the different arms. The investigation of the chromatographic behaviour of these miktoarm star polymers shall be described briefly. Two types of star polymers are investigated, namely a tri-arm polymer with one PS and two polyisoprene arms (PI), and a tetra-arm polymer with PS, PI, PB and poly(α-methyl styrene) arms.



$PS(PI)_2$ (A: PS, B, C: PI)



PS(PI)(PB)(PαMeS)

Similar to the chromatographic behaviour of linear block copolymers, the Gibbs free energy ΔG_{ABCD} of the miktoarm star polymer $A_nB_mC_xD_y$ can formally be regarded as the sum of the contributions of block A, B, C, and D, ΔG_A, ΔG_B, ΔG_C and ΔG_D respectively. P in this case is the contribution of the core of the star polymer.

$$\Delta G_{ABCD} = \Sigma(n\Delta G_A + m\Delta G_B + x\Delta G_C + y\Delta G_D) + P$$

If now chromatographic conditions are established corresponding to the critical conditions of one of the homopolymers, e.g. $\Delta G_A = 0$, and SEC conditions for homopolymers B, C, and D, it should be possible to determine the molar mass of B+C+D. Then the molar mass of A can be calculated from the total molar mass of the star polymer and B+C+D. If, instead, conditions corresponding to $\Delta G_D = 0$ are used, the molar mass of A+B+C (and, hence, D) should be accessible.

To proof this consideration, in a first set of experiments chromatographic conditions are established, corresponding to the critical point of polystyrene. Both miktoarm star polymers have PS as one of the arms. From a chromatographic point of view, PS is the most polar part of the star polymers. Accordingly, a polar stationary phase must be selected to make sure that the homopolymers corresponding to the other arms (PI, PB, PαMeS) elute in the SEC mode. As has been found in previous investigations, this situation can be established on a silica gel stationary phase using a mobile phase of tetrahydrofuran/n-hexane 43.4:56.6 % by volume. Using these chromatographic conditions in combination with a dual RI-UV detection system, the chromatograms given in Fig. 9 are obtained.

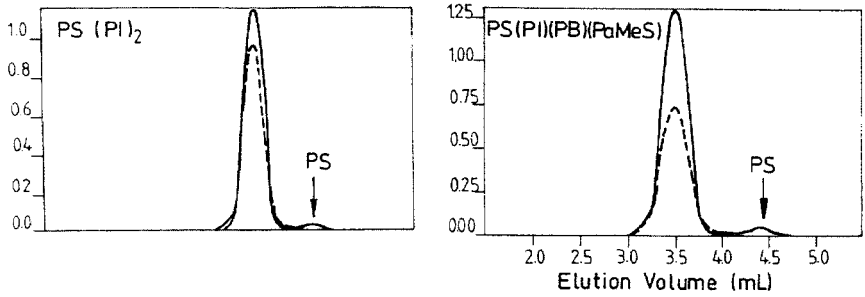


Fig. 9: LC-CC chromatograms of the miktoarm star polymers, critical conditions for PS[12)]

For both samples the major elution peak corresponds to the star polymer. In addition, a minor peak at a retention volume of 4.3 mL is detected only in the UV detector. The corresponding component is obviously low in concentration but has a high UV absorbance. A coupled LC-CC/FTIR experiment shows that this minor component is polystyrene. Accordingly, the samples contain small amounts of the precursor PS arm resulting from molecules with a deactivated polymer chain end.

In the present case, the PS arms in the star polymers are assumed to be chromatographically invisible and, therefore, do not contribute to retention. Using conventional SEC calibration curves, the molar masses of the samples are determined, see Table 2. These molar masses should be equivalent to the molar masses of the star polymers minus the PS arms. A comparison of the experimental data and the values calculated from the total molar masses and the molar masses of the PS arms shows a rather good agreement. The largest deviation is obtained for the 4-arm star polymer due to the fact that a calibration with polybutadiene does not fully reflect the hydrodynamic properties of PαMeS.

Table 2: Molar masses of the samples as determined by LC-CC at critical conditions for PS

Sample		**Calculated**	**LC-CC (PS)**	
		$\mathbf{M_n}$	$\mathbf{M_w}$	$\mathbf{M_n}$
$PS(PI)_2$	2 x PI	16,000	19,300	16,000 (PI cal.)
PS(PI)(PB)(PαMeS)	PI+PB+PαMeS	46,100	48,300	39,100 (PB cal.)

A logical next step would be to go over to chromatographic conditions, corresponding to the critical point of the homopolymer with the lowest polarity. Chromatographically this could be either PB or PI. To establish a situation where PI or PB elute at the critical point of adsorption while the other homopolymers elute in the SEC mode, a non-polar (i.e. reversed) stationary phase must be selected. The critical point of adsorption for PI corresponds to a mobile phase composition of MEK-cyclohexane 92:8 % by volume, the column temperature being 30 °C. These chromatographic conditions correspond to the SEC mode for PS and PB. The calibration curves for PS and PB are quiet different under these conditions, causing significant deviations in the calculated molar masses.

In Fig. 10, the elution behaviour of the miktoarm star polymers at the critical point for PI is presented. In both cases the main elution peak corresponds to the star polymer. Small amounts of PI can be detected in sample $PS(PI)_2$. The chromatogram of sample PS(PI)(PB)(PαMeS) indicates some higher molar mass material at the low elution volume end of the elugram. This could be an indication of a low amount of coupling products in the sample. The determination of the molar masses from the LC-CC experiments is shown in Table 3.

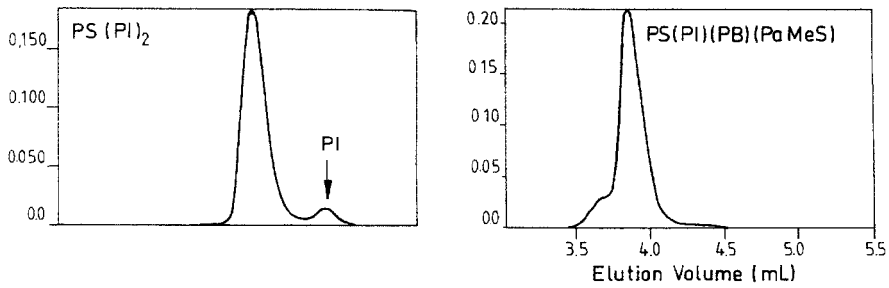


Fig. 10: LC-CC chromatograms of the miktoarm star polymers, critical conditions for PI[12)]

Table 3: Molar masses of the samples as determined by LC-CC at the critical point for PI

Sample		Calculated	LC-CC (PS)	
		M_n	M_w	M_n
$PS(PI)_2$	1 x PS	7,000	8,700	6,900 (PS cal.)
PS(PI)(PB)(PαMeS)	PS+PB+PαMeS	47,500	44,000	40,700 (PS cal.)

For sample $PS(PI)_2$ an excellent agreement of the experimental with the calculated molar mass of the PS arm is obtained since a PS calibration curve can be used. For sample PS(PI)(PB)(PαMeS) the experimental values for PS+PB+PαMeS depend on the type of calibration curve. While a PS calibration curve underestimates the true molar mass, an overestimation is obtained with the PB calibration curve. This clearly indicates that the quality of the LC-CC results in the present significantly depend on the quality of calibration, as is the case in SEC.

Acknowledgement

The contributions of J. Adrian (BASF AG, Ludwigshafen), E. Esser (Mannesmann VDO AG, Babenhausen) and I. Krämer (Südchemie AG, Moosburg,) are gratefully acknowledged.

References

1. H. Pasch, *Adv. Polym. Sci.* **150**, 1 (2000)
2. S.G. Entelis, V.V. Evreinov, A.V. Gorshkov AV, *Adv. Polym. Sci.* **76**,129 (1986)
3. S.G. Entelis, V.V. Evreinov, A.I. Kuzaev, *Reactive Oligomers*. Khimiya, Moscow, 1985
4. H. Pasch, *Adv. Polym. Sci.* **128**, 1 (1997)
5. H. Pasch, A. Deffieux, I. Henze, M. Schappacher, *Macromolecules* **29**, 8776 (1996)

6. H. Pasch, K. Rode, *Macromol. Chem. Phys.* **197**, 2691 (1996)
7. H. Pasch, B. Trathnigg, *HPLC of Polymers*, Springer, Heidelberg, 1997
8. H. Pasch, C. Brinkmann, Y. Gallot, *Polymer* **34**, 4099 (1993)
9. H. Pasch, Y. Gallot, B. Trathnigg, *Polymer* **34,** 4986 (1993)
10. J.N. Willis, J.L. Dwyer, L.M. Wheeler, *Polym. Mat. Sci.* **69**, 120 (1993)
11. H. Pasch, E. Esser, P. Montag, *GIT Fachz. Lab. Chromatogr.* **16**, 68 (1996)
12. H. Pasch, E. Esser, C. Kloninger, H. Iatrou, N. Hadjichristidis, *Macromol. Chem. Phys.* **202**, 1424 (2001)